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ON THE TRICLINIC MANGANIFEROUS PYROXENES

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The following minerals are generally regarded as triclinic pyroxenes: rhodonite, bustamite, fowlerite, iron rhodonite, sobralite, and pyroxmangite. All these mineral species represent metasilicates of manganese with smaller or greater admixtures of $CaSiO_3$, $MnSiO_3$ and $FeSiO_3$. Fowlerite also contains ZnO, but it is uncertain if the whole amount of ZnO in reality enters in the constitution of the mineral and to what extent this oxide is caused by impurities. Besides the species named babingtonite also has been considered as a triclinic pyroxene, but the relations of this compound are still but little known. According to the available analyses it differs essentially from the first mentioned minerals through the presence of a considerable amount of sesquioxides, furthermore its manganese content is restricted. On these grounds babingtonite is not included in this work.

Among the manganese-rich triclinic pyroxenes rhodonite is often found developed as good crystals, and it has early attracted the attention of mineralogists. Goniometrically it has been thoroughly investigated, and several valuable works have been written on this subject, among which may be named those of G. Flink[1] and A. Hamberg.[2] As the mineral is triclinic, the choice of crystallographic axes is arbitrary and has varied with different authors, but most frequently the similarities with the monoclinic pyroxenes have been decisive for the orientation of the crystals. This orientation is to a great extent based on the cleavage relations. As in the monoclinic pyroxenes we find in the rhodonites two perfect cleavages, intersecting each other at about 87°30′ and in addition thereto two more inferior cleavages bisecting approximately the angles of the former. Furthermore, an inferior cleavage or parting according to (001) is often present, forming an angle of about 70° with the axis of the chief cleavages, the *c*-axis. Similar cleavage relations are found in all the other triclinic pyroxenes mentioned at the beginning of this paper, though the angle of the chief cleavages deviates somewhat in the bustamites.

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[1] *Zeitschr. f. Kryst.*, 1886, Vol. **11**, p. 506.

[2] *Geol. Fören. Förhandl.*, Vol. **13**, p. 545, 1891.

On the triclinic pyroxenes a great number of analyses have been published, most of them relating to rhodonites and bustamites, the iron-rich species being more rare. On the whole the chemical relationships of the minerals must be considered rather well known. In spite of this it is a noteworthy fact that very little is definitely known about the general relations of the minerals. There are only a few reliable determinations of the optical properties and for some species they are quite lacking. Also the experimental work in the corresponding silicate systems has not been satisfactorily performed.

In the following an attempt is made at a more general treatment of the mineral group mentioned, especially as to the optical and chemical properties of the different members and as to the equilibrium relations in the system in which they fall. The very reason for this work was the discovery of a new locality of iron rich rhodonite, made several years ago by the writer at the mine of Tuna Hästberg in central Sweden.[3] The statement of the properties of this rhodonite made a closer investigation of the older known instances of related minerals in Sweden (Tunaberg and V. Silvberg) necessary and in connection with this a series of determinations on rhodonites and bustamites was started. When most of the necessary researches had been completed, the interesting paper by M. H. Hey on rhodonites and bustamites appeared.[4] In this paper a critical review of older determinations is given as also a statement on the true optical orientation. Concerning the first mentioned part of the research a reference at this place to the author named will be sufficient. Other results of a more general nature reported by Hey will be referred to in the discussion. Nearly simultaneously with the paper by Hey two publications appeared by H. Buttgenbach[5] and J. Melon[6] on the optical orientation of rhodonite. To these, too, further references will be made.

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In accordance with the custom adopted for the monoclinic pyroxenes the axis of the zone of the chief cleavages is regarded in the following discussion as the vertical *c*-axis and chosen as the central point in the stereographic projections. This orientation is maintained for all the different minerals in order to get a better general survey, although, as will be seen in the following, a different orientation would correspond better to the conditions found in the bustamites. The measurements of the relative positions of the chief optical directions were made on a universal stage. For the measurements only sections have been used which permit the orientation of two vertical cleavages within the field of observation. In most cases the sections have been cut at angles greater than 60° to the vertical zone. In exceptional cases twinning lamellae parallel to (010) or sections parallel to a cleavage have been used. As the measurements comprise data of two sets of different types to be oriented, the crystallographical and the optical, and a later transformation on the stereographic net, the errors are rather large and the various measurements seldom agree exactly with each other. Even when the material used is excellent and the crystals are cut at very favorable angles to the cleavages and the bisectrices, differences from 2–3 degrees in the coordinates are not uncommon. In less favorable cases the differences may be considerably greater. On account of this a repetition of the measurements is necessary and when possible this has been made on sections of different grains. In this way the errors are diminished and generally they would seem not to exceed one or two degrees unless the material has been inferior (showing undulatory extinction or deformation of the cleavages).

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[3] *Geol. Fören. Förhandl., Stockholm,* Bd. **52,** p. 403, 1930.

[4] *Mineral. Mag.,* Vol. **XXII,** p. 193, 1929.

[5] *Acad. Royale de Belgique, Bull. Ser. V,* T. **XVI,** 1930, p. 35.

[6] *Ibid.,* p. 66.

The measurement of the axial angles, on the other hand, can be made with considerably greater exactness (errors about 0.5°), if both the axes are accessible.

Concerning the refraction, the only exact method of determination applicable to triclinic minerals of the present type is the use of polished plates on a total refractometer. The immersion method is less reliable, since the minerals split very readily parallel to the cleavages and all the chief optical directions are oblique to them. If it was impossible to get polished plates the values recorded through immersion have been checked by using sections perpendicular to the bisectrices and by measurements of the double refraction and of the axial angle.[7]

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[7] In all rhodonites and bustamites the bisectrix γ forms the smallest angle with the axis of the vertical cleavages and is best accessible in the powder. Hence only this bisectrix has been determined in many cases, when the immersion method has been employed. α and β were calculated from the double refraction and from the axial angle.

All the determinations on refraction were made with sodium light, except in those cases where the dispersion has been measured. For the researches made with the microscope white light was used. Errors originating from the strong dispersion of the axes or of the bisectrices, were reduced through screening in the objective and when necessary also in the condensor.

The determinations of the specific gravity made for this work refer to a temperature of 20°.

The material investigated by me comes for the most part from the collections of the mineralogical department of the State Museum in Stockholm. The specimens originating there are designated by the letters RM. From Professor A. Hamberg I received from his personal collection crystals from Harstigen, corresponding to the types analyzed by him. Furthermore I received from Professor A. Grönwall the original specimens from V. Silvberg, previously investigated by M. Weibull and belonging to the collections of the Mineralogical Inst. of the University of Lund. To all the gentlemen mentioned and to the director of the Mineralogical Department of the State Museum, Professor G. Aminoff, I wish to express my cordial acknowledgments.

Most of the new analyses necessary for the investigation have been performed by the chemist of the Geolog. Survey of Sweden, Dr. A. Bygdén. For his careful work and kind assistance I am very grateful. Also to Lic. Phil. G. Assarsson, assistant chemist at the Survey, I am much obliged for his assistance in making two analyses.

Owing to the readiness with which the minerals split along the cleavages the preparation of the slides is a somewhat complicated matter, especially if the specimens used are single crystals or single crystal fragments and the section is made at a large angle to the cleavages. To get usable slides in certain cases it has been necessary to develop a method of melting the fragments in glass (ordinary Na-glass or Pb-glass, melting point about 800–900°). Most of this work was done by the preparator of the Geol. Survey, G. Larsson.

General Relations

In the triangular diagram in Fig. 1 all reliable analyses of natural triclinic Mn-rich pyroxenes known to the present writer from the literature, as well as those made for this work, have been plotted according to their content of $CaSiO_3$, $MnSiO_3$ and $FeSiO_3$, calculated as mol. per cent.[8] The natural minerals are never quite pure but hold some admixtures of MgO, often also of BaO and ZnO, the last-mentioned oxide especially being known from the Franklin Furnace specimens. Of these oxides BaO has been included with CaO. The amount of BaO is always very small and plays no part, the amount of MgO is greater, in most cases 0.5–1 and in certain cases 1.5–4.5 per cent by weight. This oxide has been included with FeO as being chemically most closely related to it. If MgO were omitted, the points on the diagram would move away from the $FeSiO_3$ corner but the displacements generally would be small and the general aspect of the diagram would not change.

The ZnO, contained in some analyses is not taken into consideration at all. This was done on the supposition that the presence of it is chiefly due to impurities of enclosed willemite grains, which cannot be avoided unless ultraviolet light is used. On the other hand, as is shown by the work of Hey and by the analysis No. 10 in this paper, the amount of the remaining ZnO, when the mineral powder is treated in this way, will be quite small and negligible.

A list of the analyses used for the diagram is given below. Of the older analyses all showing an excess or a deficit of SiO_2 greater than 3 per cent by weight, or holding considerable amounts of H_2O and CO_2 are excluded. The analyses of hedenbergite and wollastonite are taken from the mineralogical handbooks with the exception of two of the hedenbergites which correspond to the "green rhodonite" and "Herault" of the work of Wyckoff, Merwin and Washington on the pyroxene group.[9] Only hedenbergites with less than 5 per cent by weight of MgO have been considered.

1. Rhodonite, Vittinge, Finland, new, this paper No. 1, Table 1.
2. “ “, M. Saxén, *Fennia*, **45**, No. 11, p. 15, 1925.
3. “ Långban, *Hintze*, **II**, p. 1165, No. IX.
4. “ Viu at Turin, *Hintze*, **II**, p. 1165, No. V.
5. “ St. Marcel, Piemont, L. Colomba, *Atti R. Acc. Torrino*, **39**, 644, 1904.
6. “ Csucsom, *Hintze*, **II**, p. 1165, No. III.
7. “ Harstigen, Sweden, A. Hamberg, *Geol. Fören. Förh.*, **13**, p. 572, 1891.
8. “ “ “ “ “ “ “ “ “ “
9. “ “ “ “ “ “ “ “ “ “
10. “ “ “ “ “ “ “ “ “ “

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[8] The small percentages of Fe_2O_3 present in the analyses have been calculated as FeO. In some cases all the iron is determined as Fe_2O_3, but this oxide as well as Al_2O_3 is probably always subordinate in the triclinic pyroxenes.

[9] *Am. J. Sc., Ser. 5*, Vol. **10**, 1925, p. 383.

11. Rhodonite, Val d'Err, Grisons, Switzerland, J. Jakob, *Min. Mitt.*, **1923,** Vol. 3, p. 236.
12. “ Harstigen, Sweden, M. H. Hey, *Mineral. Mag.*, Vol. **XXII,** p. 193, 1929.
13. “ Harstigen, Sweden, A. Hamberg, *Op. cit.*
14. “ Långban, new, this paper, No. 4, Table 1.
15. “ “ “ “ “ “ 6, “ “
16. “ Tetela, Mexico, *Hintze*, **II,** p. 1165, No. XXVIII.
17. “ Långban, new, this paper, No. 5, Table 1.
18. Iron rhodonite, Gåsborn, Sweden, new, this paper, No. 11, Table 1.
19. “ “ Algier, *Hintze*, **II,** p. 1165, No. XXIX.
20. “ “ Tuna Hästberg, Sweden, new, this paper, No. 12, Table 1.
21. Bustamite, Tetela, Mexico, *Hintze*, **II,** p. 1165, No. XXVI.
22. “ Radautal, J. Fromme, *T. M. P. M.*, **28,** 308, 1929.
23. “ Långban, new, this paper, No. 9, Table 1.
24. “ *Hintze*, **II,** p. 1165, No. VII.
25. “ Långban, M. H. Hey, *op. cit.*
26. “ “ G. Lindström, *K. V. A. Övers.*, **1880,** 53.
27. “ Franklin Furace, new, this paper, No. 10, Table 1.
28. “ Långban, new, this paper, No. 7, Table 1.
29. “ Franklin Furnace, M. H. Hey, *op. cit.*
30. “ “ “ E. S. Larsen and E. V. Shannon, *Am. Mineral.*, 1922, Vol. **7,** p. 95.
31. Sobralite, V. Silvberg, M. Weibull, *K. V. A., Övers.*, Stockholm, 1884, No. **9,** p. 29.
32. “ “ “ new, this paper, No. 14, Table 1.
33. Sobralite+iron rhodonite, Tunaberg, J. Palmgren, *Bull. Inst., Upsala,* Vol. **XIV,** p. 172, 1917.
34. “ + “ “ “ new, this paper, No. 16, Table 1.
35. Pyroxmangite, W. E. Ford and W. M. Bradley, *Am. J. Sc.*, Ser. 4, Vol. **36,** p. 169, 1913.
36. Mn-Hedenbergite, V. Silvberg, M. Weibull, *op. cit.*

On account of the distribution of the points in the diagram and with regard to the relations found in the slides of the pyroxenes studied, an attempt has been made to sketch the stability relations in the system composed of the three pure metasilicates. The relations found are rather simple. In the triangle we find two simple compounds, rhodonite and wollastonite and in addition hereto three composite compounds, hedenbergite, bustamite and sobralite. With this latter pyroxmangite is provisionally included, though the properties of this mineral are still to a great extent unknown. The pure $FeSiO_3$-pyroxene is not known among the natural minerals, nor is it obtained in experimental researches. The curves delimiting the stability fields are given with full lines in those parts where information has been gained from the paragenesis of two or three of the minerals in the same specimen. In most of these cases the minerals appear in a graphical or homoaxial intergrowth with each other. For the rest the course of the curves is drawn approximately on account of the distribution of the analyses.

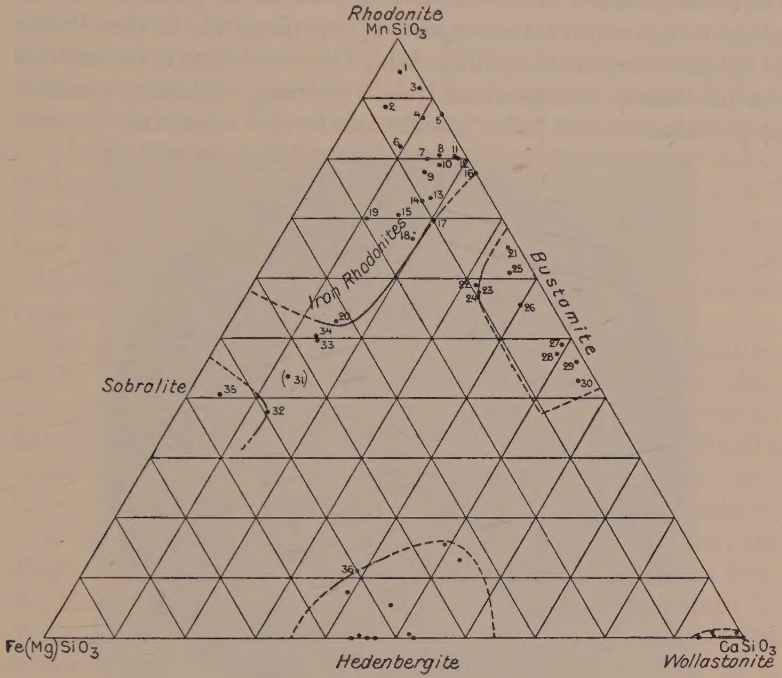

FIG. 1.

From the optical properties of the triclinic minerals described below, and from the determinations of their specific gravities, it appears that the relations between all the triclinic pyroxenes are non-isomorphic. The same holds good also for the triclinic pyroxenes and hedenbergite. With regard to the series bustamite—wollastonite, on the other hand, the relations found speak in favor of a true isomorphism, but in this series complications which will be discussed later enter and produce a discontinuity.

Rhodonite can take up Fe (Mg) SiO_3 to an extent of about 32–42 mol. per cent without losing its rhodonitic character. For those members of this series which are richer in $FeSiO_3$ than about 10 mol. per cent, the name iron rhodonite is considered to be appropriate by the present writer.[10] In no case are the iron rhodonites so far known poorer in $CaSiO_3$ than 10 mol. per cent, in most cases they contain 15–20 mol. per cent of this silicate. The highest Fe-rich iron rhodonite known is the Tuna Hästberg mineral described by the present writer in the paper just referred to (point 20 in the present diagram). It is homogeneous, but it may lie in the vicinity of the boundary of the stability field. This conclusion is drawn from the relations in the specimen from Tunaberg originally described by J. Palmgren and J. M. Sobral[11] and further examined by me in this paper. The analyses answering to this specimen are Nrs. 33 and 34. In the corresponding slides we do not find a homogeneous mineral but a mixture of three pyroxenes besides other minerals, removed from the analyzed powders by a careful separation. The

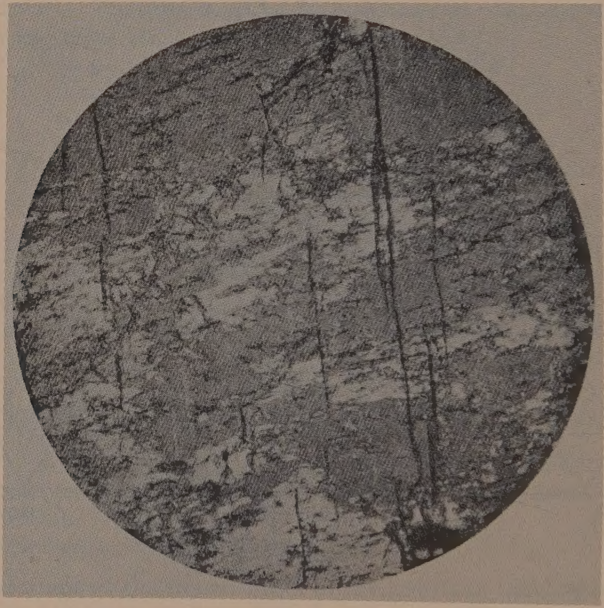

FIG. 2. Sobralite and iron rhodonite, homoaxially intergrown with each other. White=sobralite, grey=iron rhodonite. In the latter twinning lamellae parallel to (010). The partly clouded appearance of the sobralite is due to the presence of small, newly formed inclusions, probably of grünerite. The same mineral is also found as inclusions in the iron rhodonite, arranged along lines parallel to (001). Somewhat larger prisms of grünerite are seen at more points. Magn. 48×, crossed nicols.

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[10] Compare *Geol. Fören. Förh., Stockholm*, Bd. **52,** p. 403, 1931.

[11] *Bull. Geol. Inst., Upsala*, vol. **XIV,** 1917, p. 173; and vol. **XVIII,** 1921, p. 47.

pyroxenes present are iron rhodonite, sobralite and a diopsidic hedenbergite, all for the most part homoaxially intergrown with each other (Fig. 2). Of the pyroxenes the iron rhodonite is clearly present in greater quantity than the sobralite. The monoclinic pyroxene is present only in subordinate amounts. The mixture corresponding to the two points in the diagram, therefore, is not stable but has split up into three components. The place of the sobralite in the diagram is approximately stated by the analysis of the V. Silvberg-mineral (point 32) which optically is identical with the sobralite, from Tunaberg. Hence the boundary of the stability field of the iron rhodonites must be situated between the points 33–34 and the point 20 of the Tuna Hästberg iron rhodonite; and, as is shown later, the boundary of the sobralite-field is to be drawn through the sobralite-point. Thus there exists a distinct discontinuity area between sobralite and the iron rhodonites.

The unstable area between the sobralite and the iron rhodonites, on the one hand, and the monoclinic hedenbergites, on the other, must be considerably larger. According to the analysis quoted by Palmgren (referred to as No. 19 of Table 1 in this paper) $MnSiO_3$ in the diopside from Tunaberg amounts to about 6.2 mol. per cent. However, this pyroxene holds a considerable quantity of $MgSiO_3$ (20.7 mol. per cent) and belongs to a Mg-richer series than the diagram here presents. More relevant information is gained from the V. Silvberg minerals. In the specimens formerly examined by Weibull both iron rhodonite and sobralite are seen mixed with the monoclinic pyroxene named by him Mn-hedenbergite (No. 36 in the diagram), which holds 11.2 mol. per cent of $MnSiO_3$ but only 8.7 mol. per cent of $MgSiO_3$. Thus the area of discontinuity may run from the point represented by the Mn-hedenbergite to the points of the two minerals named. Of these no analysis is available of the iron rhodonite but optically it is about identical with the Tuna Hästberg rhodonite.

Rhodonite can dissolve about 20–22 mol. per cent of $CaSiO_3$, but from this limit it is not miscible with the bustamite. The discontinuity stretches from the limit named to 32–33 mol. per cent of $CaSiO_3$. The bustamites are known to contain a maximum $CaSiO_3$-content of 57 mol. per cent. The extent of the discontinuity area between the rhodonites and the bustamites is determined from a specimen received from the British Museum and originating in Långban (Nos. 5 and 9 of Table 1, Nos. 17 and 23 in the triangular diagram). In it rhodonite and bustamite are intergrown with each other in a granophyre-like manner (Fig. 3). Of the bustamite an analysis has been made previously by Hey, who kindly sent me the specimen. The two minerals, the bustamite and the rhodonite, have later been separated by me from each other and analyzed.

No case of paragenesis between bustamite and heden-gergite is known to the present writer. It is true that a chemical mixture corresponding to such a case would seem seldom to be realized in the natural rocks and mineral deposits. However, from the relations known it is evident that a discontinuity must exist. This can be concluded from the marked differences as to the optical and other properties of both the compounds. Furthermore, the quantities of iron in the bustamites are constantly very low (3.2 mol. per cent at most in the modern analyses; in one old analysis—*Hintze*, No. IV, p. 1165–, rejected for this work, FeO = 6.54 per cent by weight). In an Mg-free system the limit of the bustamite field

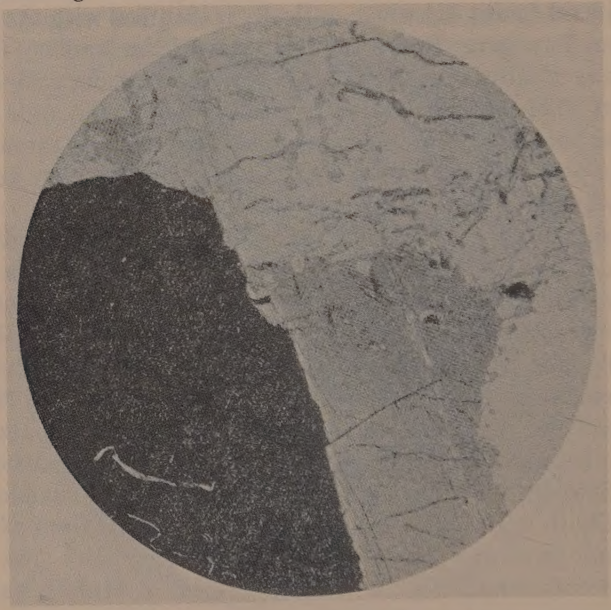

FIG. 3. Rhodonite (white) and bustamite (dark) graphically intergrown with each other. The small inclusions of a lamellar or tabular shape, occurring above the greater part of the bustamite, consist of diopside-perthite. The more irregular, partly ramified inclusions in the rhodonite in the upper part of the figure and to the right of the greater part of bustamite consist of calcite. Magn. 28×, crossed nicols.

would possibly lie at about 5 mol. per cent of $FeSiO_3$. The present point of the limit (10–11 mol. per cent) is influenced by the content of $MgSiO_3$, the effect of which is rather conspicuous on account of the low content of iron. The area of the hedenbergites, on the other hand, extends further in the direction of the bustamites, but even the most Mn-rich specimens known contain not more than 15 mol. per cent of $MnSiO_3$.

The relations of bustamite and wollastonite form a matter of great interest. When an orientation of the bustamites is chosen, which is in accordance with that of the rhodonites and the monoclinic pyroxenes, no similarities as to the crystallographical or optical properties are apparent in comparing bustamite with wollastonite. But if we choose the axis of the cleavage zone (the *c*-axis in the general orientation) as the *b*-axis, the similarities become evident. As will be shown in the discussion of the optical properties the bustamites alter their optical orientation markedly with increasing amount of CaO, and the change runs in the direction towards what is found in wollastonite. The cleavage angle of both the minerals is about 95°, but in all the other pyroxenes the angle is 91°40′–92°30′. Finally the optical properties and the specific gravity of wollastonite show a close agreement with the extrapolated values of the bustamites. Thus there are many reasons to suspect real isomorphic relations between these two compounds. Notwithstanding this, it is a remarkable fact that connecting mixtures between the two mineral species are quite lacking. The cause of this might be sought for in the absence of corresponding chemical mixtures in nature, but this argument seems not to be substantiated as the Mn-rich triclinic pyroxenes can be combined with free $CaCO_3$ and quartz or appear in carbonate layers. The real reason of the absence of intermediate forms in the series must rather be sought in the dimophism of the substance $CaSiO_3$ and the position of the inversion point in the system $CaSiO_3$–$MnSiO_3$. Of the two modifications known of $CaSiO_3$ only that which is stable at the lower temperature (below 1200°) can be regarded as isomorphous with the bustamites, the pseudo-wollastonite showing rather great dissimilarities compared with the latter. The forming of mix crystals, therefore, is restricted by the temperature limit of the inversion point, on the one hand, and by the eutectic point of bustamite-rhodonite on the other. The determination of the latter is not yet to be regarded as conclusive, but it points to about 1150°. Also if the real eutectic temperature is somewhat lower than this figure, and the position of the inversion point may be somewhat altered through the admixture of greater amounts of $MnSiO_3$, the range of temperature within which mix crystals of $CaSiO_3$ and $MnSiO_3$ are stable must be rather limited and be restricted to the vicinity of the discontinuity between rhodonite and bustamite (compare the schematic diagram in Fig. 4). The only possibility of getting mix crystals of greater Ca-content would be if the melting point of wollastonite could be realized, or if the crystallization temperature, through the influence of other substances present, could be lowered considerably below the liquidus curve and below the inversion point. The absence of corresponding crystal products shows that this is not realized in nature. The possibility of obtaining intermediate mixtures must therefore be restricted, and in spite of the

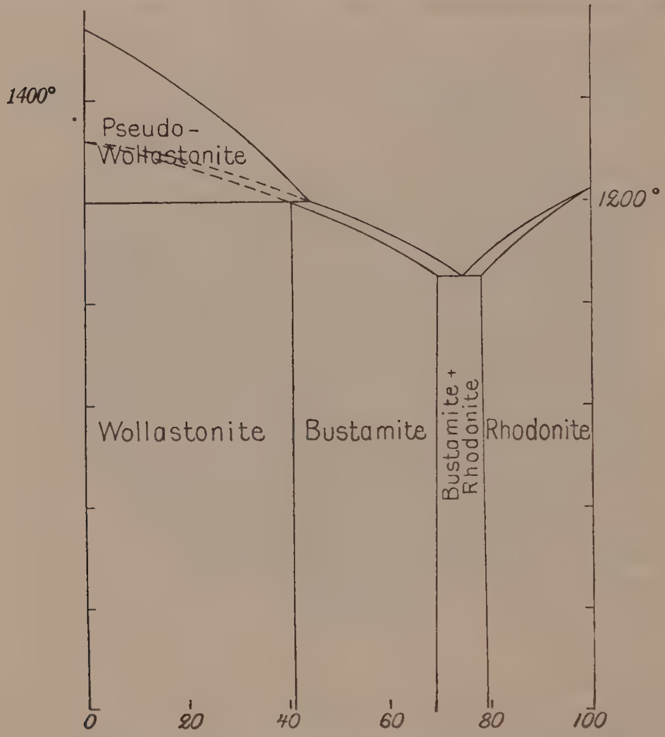

FIG. 4. Schematic diagram of the system $CaSiO_3$–$MnSiO_3$, chiefly constructed from the relations in the natural minerals.

fact that bustamite and wollastonite offer good isomorphic relations as to their properties, the corresponding system notwithstanding shows a marked discontinuity. In fact this discontinuity is greater than in any other of the binary systems present in the ternary diagram.

If these considerations are correct, the bustamites should be regarded as Mn-rich mix crystals of wollastonite rather than as independent minerals. The most convenient orientation of the bustamites should be the following: the cleavage face here designated as $(\bar{1}10)$ corresponds to (001) and the cleavage (110) to (100).

It should be remembered that the conception of a close relationship between bustamite and wollastonite is by no means new. As early as 1892 A. Hamberg[12] pointed out that the rhodonites (including bustamite) show as close relations to wollastonite as to the monoclinic pyroxenes. His opinion is based *inter alia* on the great capability of rhodonite to dissolve lime (in the bustamites). Among earlier orientations of the rhodonites those of v. Kokscharow and Des Cloizeaux are similar to that proposed here for the bustamite in choosing the axis of the vertical zone as the crystallographic *b*-axis. Recently B. Gossner and K. Brückl,[13] on the basis of researches on the atomic structure of rhodonite, have proposed an orientation differing only from that adopted by the present writer for the bustamite in using the opposite directions. However, no one of the authors named has realized the non-isomorphic relations between rhodonite and bustamite and the isomorphism between bustamite and wollastonite, nor has the chemical discontinuity between both the first named species been known previously.

The material investigated also gives some information concerning the equilibrium relations existing between rhodonite and diopside. In the specimens examined from Långban a small amount of diopside is present in most cases. This may be a Fe-poor species, because the diopsides analyzed from the Långban mines are of this type.[14] Furthermore the refraction is lower than that of rhodonite. In most cases the diopside appears as perthitically included small lath-shaped or more irregular patches, extended and arranged parallel to (001) (Figs. 5–6). The dimensions of the inclusions decrease in size to those of minute lamellar interpositions or appear also as irregular streams arranged in the manner mentioned above. In the very MgO-rich rhodonite, investigated by me, small isolated but non crystallographically arranged grains of diopside are also present. Apparently the first-mentioned (perthite-like) inclusions are due to a separation of diopside from the rhodonite in the solid state, whereas the irregularly orientated grains have separated as free individuals at the same time as the rhodonite, or earlier. The amount of the perthitically enclosed diopside is small, perhaps 2–3 mol. per cent at most. However, the separation of the mineral is not complete, some parts of the rhodonites being clouded by the inclusions, others being clear and homogeneous. The greater part of the MgO of the analyses, therefore, belongs to a homogeneous solution of rhodonite and diopside. The highest Mg-content

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[12] *Op. cit.*, pp. 552–553.

[13] *Centralbl. f. Min., Geol. Pal.*, **1928**, Abt. A, p. 316.

[14] Two analyses of W. Hissinger and G. Rose show $MgO = 16.99–17.81$ per cent by weight, $Fe_2O_3 = 2.16–2.18$, "Mn-oxide" $= 1.45–1.59$. *S. G. U.* ser. Ca, No. 23, p. 35.

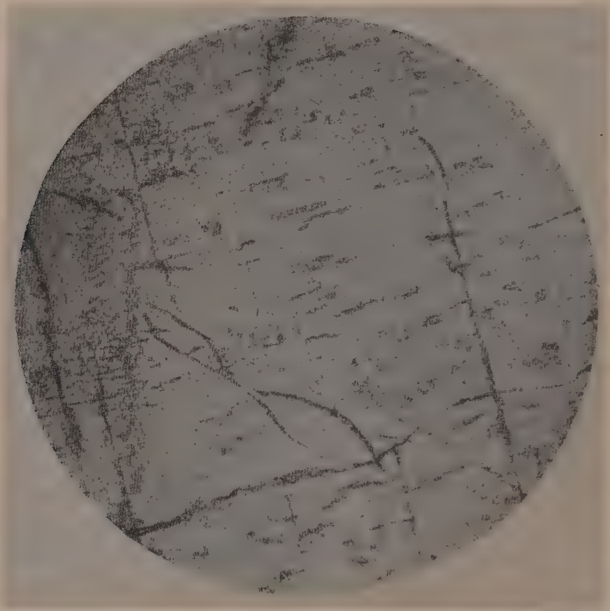

Fig. 5. Rhodonite from Långban (Specimen 2), section about perpendicular to (001) and (110), and showing traces of the cleavage according to the latter face. In the rhodonite a few isolated and irregularly bounded grains of diopside are present. Furthermore numerous smaller, lamellar inclusions of the same mineral are visible arranged parallel to (001). To the left a fissure like line is seen along which the diopside–"perthite"–inclusions are abundant. Magn. 48×, crossed nicols.

rhodonite is No. 6 of Table 1 (the same as No. 15 of the triangular diagram), and it is this specimen which holds the isolated diopside grains in addition to the perthitic inclusions. For the analysis the powder was repeatedly treated with the solution of Clerici until a quite homogeneous fraction of the powder as far as spec. gravity is concerned was obtained. Most of the "free" diopside grains may have been avoided in this manner but not the perthitic inclusions. The resulting analysis, therefore, may be considered to mark the limit of the stability field of the rhodonites at the very crystallization temperature. Its $MgSiO_3$ content is 14.2 mol. per cent. On the other hand, rhodonite No. 5 of Table 1 (the same as No. 17 of the triangular diagram of Fig. 1) holds some sparse perthite inclusions of diopside. It may lie near the limit of the stability curve at a lower temperature. Its $MgSiO_3$-content is 6.2 mol. per cent. This is the only convincing case of a separation in the solid state found by the writer in the minerals investigated. It should be mentioned that no similar perthitic separation products are found in

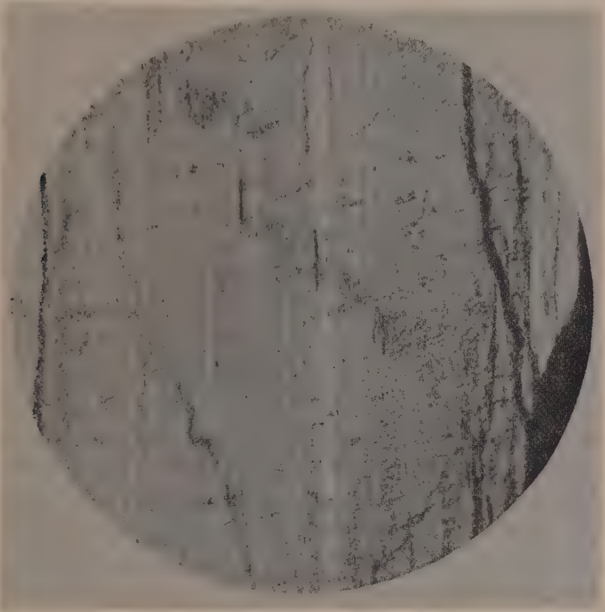

FIG. 6. The same rhodonite as in FIG. 5. Section about perpendicular to α. The white lines represent twinning lamellae parallel to (010). The rhodonite holds the same diopside-perthite-inclusions as in Fig. 4, and similar perthite-rich lines as in the latter. Magn. 48×, crossed nicols.

the bustamites. Also in the specimens answering to Nos. 5 and 9 of Table 1, in which the bustamite is graphically intergrown with rhodonite, the former is homogeneous though the rhodonite holds perthitic segregations of diopside. In both minerals the amount of MgO is similar (MgO = 5.9 and 6.2 mol. per cent). The solubility of the diopside, therefore, is greater in the bustamites than in the rhodonites.

This conclusion is valid only for the Fe-poor rhodonites. In the iron rhodonites the Mg-content is greater (up to 6 mol. per cent of $MgSiO_3$) without any separation of the Mg-component.

If we altered the diagram of Fig. 1 so as to form a tetrahedron and placed $MgSiO_3$ at the top, we should get a complete picture of the system of the sesquioxide-free natural pyroxenes. Thanks to the works of earlier authors, especially to those of R. B. Sosman[15] and B. Asklund,[16] we can imagine some of the chief features of the distribution of the minerals in it. Along the $FeSiO_3-CaSiO_3-MgSiO_3$-side we should get a continuous space area between hedenbergite, diopside and enstatite-clino-enstatite with the exception of a discontinuous area in the vicinity of the $MgSiO_3$-corner. The mentioned area of orthorhombic and monoclinic pyroxenes is in all probability separated from the areas of wollastonite-bustamite through a discontinuity area which extends to the corresponding gaps between bustamite-rhodonite and between iron rhodonite and sobralite. Whether any separate smaller mineral groups are situated in the interior of the tetrahedron, we do not know as yet. On account of the relatively low percentage of MgO in all the triclinic pyroxenes analyzed it does not seem probable that the stability areas of them will rise to any greater heights in the tetrahedron.

An artificial mineral perhaps related to the iron rhodonite or to the sobralitic group is the triclinic vogtite described by C. Hlavatsch[17] and A. F. Hallimond[18] from slags. However, the position of the mineral is not clear from the facts available. The analysis of Hallimond shows the following ratios of the chief oxides: $MnSiO_3 = 21.75$, $FeSiO_3 = 30.43$, $MgSiO_3 = 15.67$, $CaSiO_3 = 32.14$ mol. per cent.

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[15] *Journ. Wash. Acad. Science*, **1911**, 1, p. 86.

[16] *S. G. U., Ser. C*, No. **325**, p. 75. A diagram of the natural rock forming pyroxenes had already been compiled considerably earlier by H. E. Johansson (compare Asklund, p. 76).

[17] *Zeitschr. f. Krist.*, **42**, 1906–1907, p. 590.

[18] *Mineral. Mag.*, vol. **XVIII**, 1919, p. 369.

In the ternary diagram examined by me no series of unlimited solutions are represented, if we ignore the possible exception of the wollastonite-bustamite series. The type of equilibrium applicable in all other cases would be Roozeboom's No. V.

All the results outlined above refer to the natural minerals and to the relations in natural mineral mixtures. The results obtained in this way need not be similar to those obtained in artificial melts, as the crystallization temperatures in the natural systems will generally be lowered through the presence of other substances. In those cases where the distances of unmixing are small, as in the bustamite-rhodonite and iron rhodonite-sobralite systems, it might be suspected that the equilibrium type belonging to the melting temperature would be that of Roozeboom's No. III and that the discontinuity would not enter until a lower temperature is reached. This is possible, and then we should get equilibrium relations corresponding in principle to those of the alkali feldspars. A statement covering this question and of the lower temperature limit where possibly there exists unlimited mixing power, should be of great interest.

With the exception of the perthite-like inclusions of diopside in the rhodonites from Långban nothing is seen in the specimens studied which with any probability would indicate a splitting up of the components in the solid state. In the case of the intergrowth between bustamite and rhodonite, described from Långban, the minerals form a coarse, not homoaxial intergrowth which may best be called graphical. In the mineral mixtures from V. Silvberg, alluded to in the foregoing, the pyroxenes occur as separate grains. In the specimen from Tunaberg we find the following relations: the greater part of the iron rhodonite and all the sobralite are homoaxially intergrown. In addition we find a minor quantity of pure iron rhodonite. The diopside is for the most part homoaxially intergrown with the composite sobralite-iron rhodonite individuals, but rare grains of free diopside seem also to be present. These relations are best interpretated as due to a crystallization according to a system of limited solubility of the type indicated by the triangular diagram of Fig. 1.

Artificial rhodonite has been prepared by more workers and seems not to be difficult to obtain. According to F. Doerinckel[19] it melts incongruently at 1215°. P. Lebedew[20] gives the melting-point at 1210°. F. M. Jaeger and H. S. Van Klooster found it at 1273°.[21] Researches on the melting-points and on some of the crystallization products obtained in the system $MnSiO_3-CaSiO_3$ have been made by A. S. Ginsberg[22] and S. Kallenberg.[23] Both of them found similar relations and according to them the original crystal products would form a continuous series of homogeneous compounds. A feebly marked minimum appears at 10–13 mol. per cent of $CaSiO_3$ at 1150°–1184°. Thus the corresponding type of equilibrium would be No. III. The melting point of rhodonite was found to be 1218° (Ginsberg) and 1180° (Kallenberg). The former figure is in close agreement with that of Doerinckel and Lebedew. The melting-point of $CaSiO_3$, according to the results of the Geophysical Laboratory, is 1540°.

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[19] *Metallurgie,* **1911**, p. 201, quoted by H. E. Boeke, *Grundlagen d. phys.-chem. Petrographie,* **1915**, p. 193.

These results seemingly agree with the conception that the bustamites are a Mn-rich series of wollastonite mix crystals. On the other hand, they do not show any traces of the complications introduced through the dimorphism of the $CaSiO_3$ component, nor does there appear to be any manifestation of discontinuity between rhodonites and bustamites. On the other hand, the researches on the crystalline products are not complete.

According to Kallenberg, pure $MnSiO_3$ forms homogeneous mix crystals with $FeSiO_3$ to an extent of about 50 mol. per cent of the latter.[24] Melts richer in iron could not be prepared on account of the reduction or oxidation of the iron. The results gained are in fair agreement with the relations found in the natural minerals, the critical mixtures beginning at 32–40 mol. per cent of Fe (Mg) SiO_3.

The artificially prepared rhodonite has been examined optically be several writers, though no exhaustive description of it has been given. Most reliable are the values of the spec. gravity and they vary between 3.63 and 3.716. The value given by Jaeger and Van Klooster (3.716) agrees fairly well with the figure calculated for the pure natural rhodonite (3.727). Ginsberg gives the refraction as 1.74. This would correspond to β in natural rhodonite (1.741), Kallenberg found $2V_\gamma$ rather small. The angle of natural rhodonite is about 57.5°. Evidently the crystal products obtained by the authors named are identical with the natural rhodonite.

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[20] *Zeit. f. Anorg. Ch.*, Vol. **70**, p. 313, 1911.

[21] *Proc. Akad., Amsterdam*, Vol. **XVIII**, p. 908, 1916.

[22] *Zeitschr. Anorg. Ch.*, **1908**, Vol. 59, p. 346.

[23] *Zentralbl. Min., Geol. Pal.*, **1914**, p. 388.

[24] *Zeitschr. Anorg. Ch.*, **1914**, p. 362.

In an interesting paper published in 1927 A. N. Winchell discussed the relations of the triclinic pyroxenes.[25] The opinion is put forward that the rhodonites, bustamites, sobralite and pyroxmangite are all independent minerals or mineral groups. This reasoning is based on the valuable work of Wyckoff, Mervin and Washington[26] on the atomic structures of the different pyroxenes. Winchell's opinion is confirmed, on the whole, by the present investigation. The relations given in the triangular diagram of Fig. 1 agree well with the grouping of the pyroxenes made by the three writers mentioned on the basis of the atomic structures; but the provisional assembling of sobralite and pyroxmangite in one and the same group, made by me, is not in accordance with the respective X-ray patterns found. On this point it is to be remarked that if the X-ray examination of the sobralite was made on powder of the Tunaberg specimens, it must refer to a mixture of pyroxenic minerals of which two are triclinic (sobralite and iron rhodonite) and one is hedenbergitic diopside.[27] And the mode of distribution of the pyroxenes, as shown in the above, is of such a character that no one of them can be obtained in the pure state. The paper of the writers mentioned does not indicate whether this fact has been considered. Finally, the optical properties of the pyroxmangite are only partially known.

In the paper by M. H. Hey referred to above the series rhodonite-bustamite is considered as continuous. A similar opinion has also recently been expressed by N. H. Magnusson[28] in his paper on the Långban mines. However, no facts in favor of the opinion expressed are quoted by the last named writer. Hey bases his conclusion of the continuity in the series on three specimens examined by him and on determinations of earlier authors. However, when we consider the small distance of discontinuity in the series, it is apparent that the number of reliable determinations at the disposal of Hey was too small to allow of a true statement of the matter.

(*To be continued*)

[25] *Am. Mineralogist*, **1927**, p. 10.

[26] *Am. Journ. Sc.*, Ser. 5, vol. **10**, 1925, p. 383.

[27] In addition thereto the specimens contain considerable amounts of other minerals.

[28] *S. G. U.*, *Ser. Ca.*, No. **23**, 1931, p. 44.

THE RELATIONS OF THE GRENVILLE SEDIMENTS AND THE POTSDAM SANDSTONE IN EASTERN ONTARIO

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Introduction

The Grenville Sub-Province includes that part of the Canadian Pre-cambrian lying in eastern Ontario, extending north and east into Quebec. It also takes in the Adirondack region in the United States.

The major part of the Grenville area is underlain by two main rock series. The oldest, is a series of altered sediments known as the Grenville formation. These rocks are highly metamorphosed and now consist of banded quartzites, gneiss, and schist, interbedded in places with crystalline limestone.

The Grenville series, probably already altered and folded during early Pre-cambrian time, was invaded by a second and younger series of batholithic intrusives, consisting of granite, syenite, and pegmatite. Contemporaneous with this intrusion a further disturbance of the sediments again subjected them to folding and alteration. In places the sedimentary beds were pushed aside by the batholithic masses or dykes. Other and more intimate phases of invasion along the bedding produced the lit-par-lit structure so common in the area. During this movement the sediments were metamorphosed into gneiss, quartzite, and crystalline limestone. The remnants of bedding are still visible. Both the strike and dip vary locally; the series now has a dip of from 70° to 90°. The strike is northeast. Where folding has taken place it is consistent for all phases, the folds of quartzite, limestone, and gneiss being similar in type.

The main phase of the intrusive is a coarse grained red granite, containing milky blue quartz, red feldspar and hornblende. Syenite and pegmatite are other phases common in the area but are less abundant than the granite. The disturbance and alteration are regarded as late Pre-cambrian. An extended period of erosion at the end of Pre-cambrian time has truncated the folds and completed base levelling.

The Potsdam sandstone was formed from the material supplied by this base levelling process, and was laid down on the eroded Pre-cambrian surface. Various Paleozoic sediments followed. Subsequent erosion removed the later formations exposing the base levelled Grenville gneisses in much the same condition as they existed at the close of Pre-cambrian time.

CHARACTERISTICS OF THE HEAVY RESIDUAL GRAINS OF THE POTSDAM SANDSTONE

The most striking characteristic of the Potsdam sandstone is its high silica content. Four determinations for silica from samples obtained from widely separated exposures show:

1—SiO_2—99.40 per cent
2—SiO_2—99.14 "
3—SiO_2—99.71 "
4—SiO_2—98.99 " Average $SiO_2=99.31$ percent.

The sand grains are thus nearly all pure quartz with siliceous cementing material. A small amount of calcium carbonate is found also as a cement, and in places iron oxides perform this function to a minor extent, coating the grains, and supplying the color to the red sandstone found in the district.

Most quartz grains show pronounced wear and the majority show evidence of secondary growth in a direction corresponding to the original orientation. In a general way the abundance of heavy residual grains and the number of mineral types for each sample showed a remarkable lack of variation. The sandstone from Glenburnie road near the Rideau River yielded slightly more heavy grains than the other samples examined. More minerals were identified in it than in any of the others. The grains of this sand are much more angular than in the others, and on the whole suggest less perfect sorting, and perhaps less transportation. In this sample, one flaky mineral of hexagonal outline with good basal cleavage was not determined. It is rather abundant in this one sample, but does not appear in any of the others. It is badly altered, and no pieces free from alterations could be obtained for satisfactory identification. The minerals other than quartz are not abundant nor the number of species large.

The following were identified and are listed in order of abundance (this result was obtained by an attempt at counting the number of mineral grains): Quartz, zircon, magnetite, titanite, tourmaline, apatite, rutile, garnet. Calcite and pyrite were also noted; both are considered to be of secondary origin.

The following arrangement represents the relative amount of rounding and wear exhibited by the grains.

Zircon, extreme wear, grains spherical and ellipsoidal.
Quartz, extreme wear, grains spherical—ellipsoidal, some irregular.
Apatite, extreme wear, grains mostly ellipsoidal, some irregular.
Magnetite, variation from spherical grains to fairly sharp crystal outlines.
Tourmaline, variation: Spherical forms to flat irregular but rounded pieces, some pieces show evidence of crystal outlines.
Garnet, variation: Spherical forms to fairly well preserved crystals.
Rutile, variation: Spherical forms to sharp crystal outlines.

These two lists show zircon to be the most abundant, the most consistently present, and the most rounded mineral occurring among the heavy residual grains. Most of the zircon grains have ellipsoidal or spheroidal forms; more rarely the shape is irregular and distorted. All grains are nearly colorless; some are of a very pale amber shade. They vary in size from a length of 1 mm. to .6 mm. The frosting on the zircon grains is most pronounced and consistent.

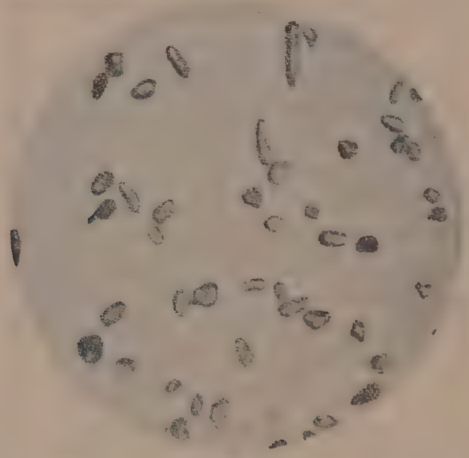

Fig. 1. Rounded sand grains. Potsdam sandstone. Note curved zircon grain above center of picture.

Considering all the heavy grains collectively, pronounced wear is general. In preparation of the samples a relatively small number of grains were split and where such fractured pieces were noted with the remaining part showing a rounded, smooth surface, they were regarded as broken during grinding. No grains of zircon could be found which displayed fresh faces and rarely did any exhibit the remnants of former crystal outline. Many grains, however, show elongation, and in such cases bent grains are not infrequent. (Fig. 1.)

Many of the zircons are so worn that they appear as small spherical grains. The distortion of the zircons is no doubt due to the folding of the host rock before the grains were released by erosion.

The relative amount of wear to which the heavy residuals have been subjected is no less significant than their abundance or persistence. This characteristic is shown best by zircon and to a nearly equal extent by titanite. By far the greater number of quartz grains show evidence of extreme wear, and most grains approach spherical or ellipsoidal form. Irregular shapes partly rounded are less common. The remainder of the minerals occur in both rounded and irregular shapes. The magnetite and the rutile in the Glenburnie road sample show practically all the stages of wear, from fresh crystal shapes to much worn grains. Some quite perfect octahedra of magnetite were recovered from sandstone obtained from Cushendall and from Bass Lake.

Apatite occurs in various worn shapes both rounded and irregular but never as sharp crystal forms. Garnets show a transition in wear between the two extremes of perfect crystals and much worn grains.

The frosting and pitting of the sandstone heavy residual grains is consistent throughout all samples and in general varies directly with the amount of rounding to which the grains have been subjected. For this reason zircon grains show the best examples of frosting.

HEAVY RESIDUALS IN THE GRENVILLE GNEISS

Examinations were made of five samples of the Grenville gneiss. In the method of obtaining samples and of recovering the heavy minerals the same procedure was followed as with the sandstone.

The number of mineral types obtained from the gneiss is decidedly greater than in the sandstone. The minerals recognized are as follows:

Quartz
Zircon
Titanite
Enstatite
Apatite
Corundum
Garnet
Pyrite
Magnetite
Hornblende
Epidote
Calcite
Biotite
Cyanite
Rutile
Microcline
Andesine
Oligoclase
Tourmaline
Sillimanite
Andalusite
Chlorite
Kaolin

Several other minerals were recovered, but not identified because grains were not obtained which were suitable for determination.

Most of the minerals occur as irregular, angular grains. Zircon and titanite are rounded, apatite less commonly. These three minerals are the only types to show abundance of rounded forms. There are also fresh types having no evidence of wear with well-formed crystal faces (Fig. 2).

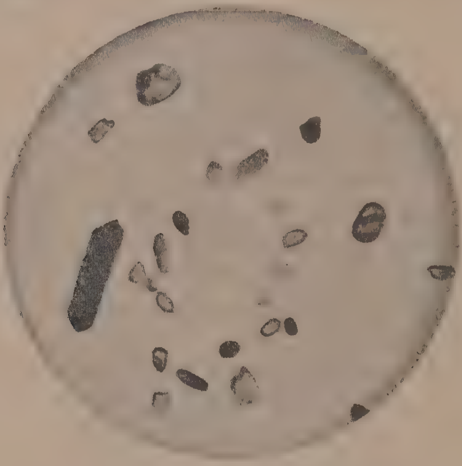

Fig. 2. Sand grains from Grenville gneiss.

Inclusions of Gneiss in Crystalline Limestone

An interesting detail of the Grenville formation is the presence of inclusions of gneiss contained in beds of crystalline limestone. These have been described by M. B. Baker as follows:

> "Of very frequent occurrence is a pseudo-conglomerate, composed of fragments of rusty weathering gneiss in a matrix of crystalline limestone. This might be mistaken as evidence of an unconformity showing the gneiss to be an older series. A close examination of the inclusions, however, shows that they are fragments of beds of para gneisses, which were mashed up with the limestones during their metamorphism—the softer limestone flowed around the pieces of gneiss and these moved like phenocrysts in a porphyry so that they often show a flowlike alignment."[1]

Samples of these inclusions were obtained and the heavy minerals recovered from them. An examination showed the presence of distinctly rounded sand grains (Fig. 3). No doubt these are waterworn grains of the original sediment preserved in the gneiss and retaining their identity. These inclusions of gneiss are not so hard and quartzitic as the main mass from which they were derived. Reactions between the constituents of the gneiss and the limestone has resulted in the formation of tremolite, augite, and other calcium silicates. Augite was recovered from these inclusions in the form of rounded grains, evidently the result of alteration, with the retention of the original rounded waterworn forms.

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[1] Baker, M. B., Geology of Kingston and Vicinity, *Ont. Bureau of Mines*, Vol. **XXV**, Pt. III.

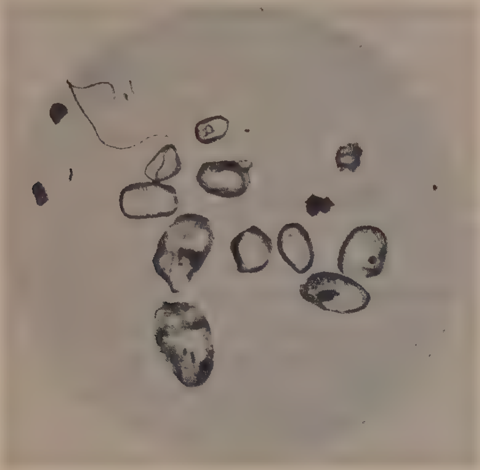

FIG. 3. Sand grains from inclusions of Grenville gneiss in crystalline Grenville limestone.

SOURCE OF THE MATERIAL OF THE POTSDAM SANDSTONE

Every heavy mineral found in the sandstone was also recovered from the gneiss. The garnet in the two formations is of the same type. Also the similarity of the zircon grains in Potsdam sandstone and Grenville gneiss is good evidence that the transportation has not been extensive, and that the sandstone lies on part of the same basement from which its material was derived. Since the Potsdam shows evidence of thorough sorting, and the material is so near its source of origin, it seems reasonable to believe that the gneisses from which in most part the Potsdam was derived are arenaceous sedimentary beds which, having experienced one cycle of erosion, were capable of supplying waste material already high in quartz and low in other minerals.

Climatic conditions in this erosion period are problematical. The presence of frosting on sand grains and the ferric oxide in layers of interbanded red and white sandstone suggest intervals of arid and probably desert conditions with stretches of wind swept coast land between the mountains and the sea.

Undoubtedly worn shapes are the result of abrasion and are therefore also the result of transportation, yet in measuring the extent of transportation, such grains, after having once become well-rounded, would not likely be much altered in shape by further transportation. Daubrée[2] states that from experiments which he performed he could prove that fresh angular sand grains subjected to 15½ miles of average river transportation became so worn that they could not be distinguished from ordinary river-worn grains. This distance seems remarkably short. It seems reasonable to assume, however, that in the initial stages of transportation, rounding may have a ratio to distance which would lose significance once the grains have become well rounded, and therefore could not be relied upon as a means of measuring distance in cases of far-reaching transportation.

The same reasoning applies to frosting. Once a sand grain has been thoroughly frosted, further effects cannot be measured. Under proper conditions, rounding and frosting may be perfected in a very short time. Window panes along sandy seashores lose their transparency in a few days, and in some instances are entirely worn through in a month, due to sand abrasion.[3] Such illustrations are convincing evidence that sand abrasion works rapidly, and that the effects on the grains themselves may result in rounding and frosting during a comparatively short period.

SUMMARY

The examination of the Potsdam sandstone and Grenville gneisses show:

1. A low content of heavy minerals with thorough rounding.
2. A similarity in kind of grains in both gneiss and sandstone.
3. The zircons especially are more perfectly rounded in the sandstone than in the gneiss.
4. The gneisses are undoubtedly sedimentary in origin and originally sandstones, shales, etc. Some igneous material has been introduced in places but commonly this is easily recognized.

CONCLUSIONS

The gneisses were sediments formed by normal erosion so that the heavy minerals were fairly well rounded.

The sandstones were formed from the gneisses rather than directly from igneous rocks. This conclusion is based on the small amount of heavy residuals as compared with quartz, and on the perfection of rounding of the zircon.

[2] Daubree, *Geologie—Experimentale*, p. 256.

[3] Pirsson and Schuchert, *Introductory Geology*, p. 13.

STRUCTURES OF SOME SILICATES

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Introduction

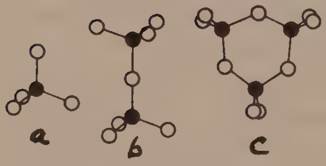
Since 1926 a large number of structures of silicates have been investigated. Though W. L. Bragg (37) has published a long paper recently on the progress of this work it may not be amiss to review his work in this journal and include in addition those structures which have been determined in the last eighteen months. It is not the intention of the writer to show projections of these structures. In the first place, they are so complicated that photographs of models or perspective drawings do not convey the proper conceptions. Secondly, they might be too technical for the reader who has not specialized in this type of study. Instead of showing such projections, an attempt will be made to develop structural diagrams which will give the student the proper conception of the structural combinations so far encountered in the silicates. Acknowledgment of the sources from which the writer has drawn is made in the bibliography. The references are necessarily limited to the latest complete *x*-ray studies of the silicates. For additional references the reader will find it necessary to consult each original investigation.

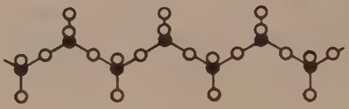
Valency and Coordinates

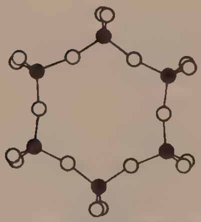
Two years ago the writer reviewed the literature of a number of simple type structures in this journal (38) and showed how each atom or ion—the silicates are most probably built up of ions—tries to surround itself with ions of opposite charge in such a manner that all bring their maximum influence to bear on one another. We might say that their spheres of influence are in contact. The radii of these spheres are significant but more important are the ratios of the radii of the cations to those of the anions which surround them. In the common silicates the cations are usually smaller than the most abundant anion O. Table I lists the radii of the most important ions in silicates. The cation of Si is so small that it just fits into the void between four anions of O which are in contact in such a fashion that their centers are at the corners of a regular tetrahedron whose edge is 2.6–2.7 Å in length. (Fig. 1, a.) The group SiO_4 thus formed is the foundation of all investigated silicate structures including quartz and other SiO_2 modifications. The SiO_4 tetrahedra may be slightly distorted but as a whole they are the most regular and reliable building units of the silicates. Si in an SiO_4 group has four valency coordinates (38) linking Si to four O. The SiO_4 group has four excess negative charges by which it is linked to neighboring cations. These may be Si or other elements.

Table I. Effective Radii of Ions of Some of the Elements in Silicates

Be^{++}	0.34 Å	Ca^{++}	1.06 Å
Si^{++++}	0.39	Sr^{++}	1.27
Al^{+++}	0.57	K^{+}	1.33
Ti^{++++}	0.64	Ba^{++}	1.43
Fe^{+++}	0.67	O^{--}	1.32
Mn^{+++}	0.70?	F^{-}	1.33
Mg^{++}	0.78	$(OH)^{-}$	1.4–1.5
Li^{+}	0.78	S^{--}	1.74
Fe^{++}	0.83	Cl^{-}	1.81
Zn^{++}	0.83		
Sc^{+++}	0.83		
Zr^{++++}	0.87		
Mn^{++}	0.91		
Na^{+}	0.98		







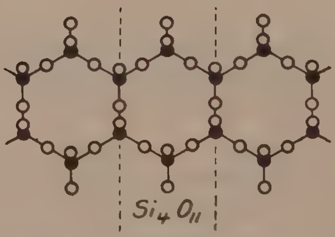


Fig. 1. (a) SiO_4 group; (b) Si_2O_7 group; (c) Si_3O_9 group (benitoite ring). After W. L. Bragg.

Fig. 2. Si_6O_{18} group (beryl ring).

Fig. 3. SiO_3 endless chain in pyroxenes.

Fig. 4. Si_4O_{11} endless chain in amphiboles.

In orthosilicates, SiO_4 groups are never in direct contact with one another. This arrangement had been suspected long ago. There had also been vague predictions of certain linkages of SiO_4 groups, some of which have lately been shown to exist. How two SiO_4 tetrahedra may have one corner in common forming an Si_2O_7 group is shown in Fig. 1,b. This grouping exists in the melilite silicates. Fig. 1,c shows a linking of three SiO_4 groups giving one large Si_3O_9 aggregate as found in benitoite. A ring of six SiO_4 tetrahedra (Fig. 2) resulting in an Si_6O_{18} group has been discovered in beryl.

Still more interesting are the endless chains of SiO_4 groups. Single chains (Fig. 3) exist in the pyroxenes (8). Due to this linking of the tetrahedra the ratio of Si:O becomes 1:3, which is that of the metasilicates. The discovery by Warren (15) of endless double chains (Fig. 4) in the amphiboles has added much to the understanding of these complex structures. The unit Si_4O_{11} occurs in them as will be shown later. Endless sheets of SiO_4 groups in which three of the four tetrahedral corners of each SiO_4 group are linked to adjoining SiO_4 groups are shown in Fig. 5. They give rise to Si_4O_{10} units as in the micas and talc. Another complex type of SiO_4 grouping is the feldspar type first predicted by Machatski (14). It consists of frameworks of SiO_4 groups. (Fig. 6.) Each tetrahedron shares its four corners with four adjacent SiO_4 tetrahedra resulting in a ratio 1:2 for Si to O.

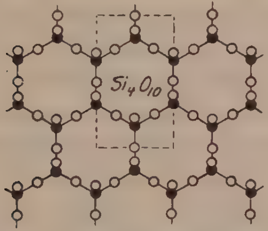


FIG. 5. Si_4O_{10} endless sheet in micas.

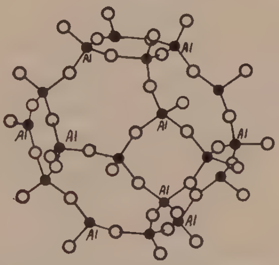


FIG. 6. $Si_6Al_6O_{24}$ framework in sodalite, after Jaeger.

Cations other than Si may have four or more valency coordinates. Their coordinate number seems to depend less on chemical valency than on their sizes and more complicated factors, some of them little understood. Aluminum may be the center of a tetrahedral AlO_4 group which strongly resembles the SiO_4 group. It is, however, slightly larger and more distorted on account of the larger size of the Al cation. Aluminum frequently is the center of a somewhat distorted octahedron in which position it has a valency of six valency coordinates to the six corners of the octahedron. These corners are the centers of O, F, or OH anions as a rule. The behavior of Al shows that an element may have more than one coordinate number even in the same structure as will be shown in andalusite, for example, in which half of the Al ions have the coordinate number 5, the other half the number 6. Mg, Fe^{II} and Na usually behave like Al with six coordinates, while Ca more often has eight coordinates. Beryllium on the other hand, is at the center of a tetrahedron like Si. Boron behaves the same way though it may have only three coordinates. The reader may have noticed that as a general rule the larger cations have the larger number of valency coordinates. This is a natural consequence of the empirical law stated earlier that each cation tries to gather as many anions about itself as will closely fit around it.

Notwithstanding the fact that in crystals an ion with a certain chemical valency may be replaced by one with a different valency, the total positive and negative valencies must balance in any stable structure. Pauling has gone farther and has proposed his "rule of compensation of electrostatic valency" (36) which has been found valid within certain limits for the structures investigated. It states that in a stable structure, the electric charge of each anion is approximately or exactly compensated by the strength of the electrostatic valency bonds reaching it from the cations to which it is linked directly. An example will illustrate this rule In olivine (forsterite) each O ion is linked to one Si and three Mg ions. Si has a valency 4, and each of its four bonds has a value 1. Mg has a valency 2. Each of its six coordinates is equal to one-third of a positive charge. The two negative charges of O are compensated exactly by $(3\times\frac{1}{3}+1)=2$ positive charges.

It is a curious observation that in an actual structure, places of weakness seem to occur only where the value for each bond sinks below a certain limit. Bonds with an individual valency of 1 appear to be extremely strong. The writer has been unable to find a structure in which cleavage, for example, cuts through such bonds. It seems also that three bonds of one-third valency each are not as strong as a single bond with a valency of 1. More observations will be necessary, however, before a definite statement can be made.

Isomorphous Replacement

A vast amount of work has been done on isomorphous replacements in silicates. We shall mention only those points of the subject which seem to have been definitely established as facts and summarized by W. L. Bragg (37). There seems to be little doubt that the amount of O in a silicate is practically a constant and should be treated as such. The O ion is so large that it is improbable that additional O ions could enter a stable structure. The F ion or the OH radical which are of about the same size as O, could possibly take its place, but it is more common for F to replace OH, or vice versa. The replacement of one cation by another is extremely common in silicates. We only need to mention the plagioclase feldspars in which Na and Si are replaced by Ca and Al, respectively. It is not possible, however, for Ca to replace Na without a corresponding substitution of Al for Si. How complicated such replacements may be is illustrated in Warren's paper on the amphiboles (16) in which a number of recast analyses are given. Mauguin's (34) investigation of the micas had shown as early as 1928 that the number of O ions in the unit cell remained practically constant. The greatest possible variation exists in micas, however, not only in the amount of substitution of one metal for another, but also in the number of metals that may replace one another. The metals which are difficult to assign in the determination of a structure are those whose cations have two different coordinate numbers. Aluminum is a typical example. It frequently takes the place of Si with four coordinates, but it may also replace Mg, Mn, Fe^{III}, Ti and Cr with six. Table I which gives the radii of common ions is helpful in this respect. An ion will replace another only if the difference between their radii is relatively small.

Structure Diagrams

Many attempts at devising correct structural formulas for silicates have appeared. Actual determinations of the structures have invalidated most of them. Nothing would be gained by listing at this time even the more valuable contributions which preceded the *x*-ray study of silicates. A structural formula can indicate only a limited number of the important features of a structure. An attempt, therefore, has been made to draw diagrams which combine the advantages of structural formulas with those other features essential for an understanding of a particular structure. It is realized, of course, that the diagrams presented are not the only possible ones which can be devised.

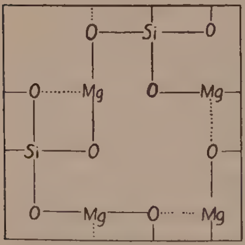
One chemical molecule, or at the most two, have been used in each figure. Ions which are not directly linked in the actual structures are kept apart in the diagrams. Since it is impossible to separate individual molecules in the structures without having unsatisfied valencies left over, "loose" bonds are also found in the diagrams. The latter are drawn in such a way that an indefinite number of them may be linked together in the principal directions without destroying the integrity of the structures. The continuity of a structure may be represented in this manner.

For simplicity's sake, not all coordinates are drawn except where absolutely necessary. Silicon and aluminum with a coordination of 4, however, always have all coordinates shown. Magnesium and aluminum with 6 coordinates frequently will have only three bonds shown. A number of bonds are drawn as full lines, others as dotted lines. *No essential structural difference exists between these two kinds.* The number of full lines to an ion indicates the chemical valency of the ion while the dotted lines are added to complete the number of valency coordinates which can be shown advantageously in the diagrams. A new feature is introduced in the chemical formulas under the diagrams. The number of valency coordinates for each element is written above the symbol of that element. Where two numbers are given some of the ions have a different coordinate number from others of the same element. The number of diagrams which could be included was limited by the cost of the cuts involved.

STRUCTURES

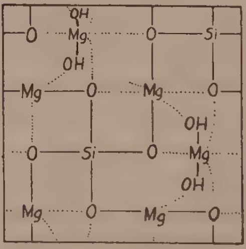
ORTHOSILICATES

In orthosilicates the ratio Si:O is 1:4 or greater. The SiO_4 tetrahedra are separated from one another by the remaining cations of the structure which will just neutralize the negative charges of the SiO_4 groups.



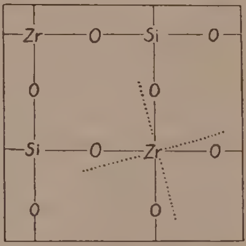
$2[\overset{6}{Mg_2}\overset{4}{Si}\overset{4}{O_4}]$

FIG. 7. Forsterite.



$2[\overset{6}{Mg}\overset{3}{(OH,F)_2}\overset{6}{Mg_2}\overset{4}{Si}\overset{4}{O_4}]$

FIG. 8. Norbergite.



$2[\overset{8}{Zr}\,\overset{4}{Si}\,\overset{3}{O_4}]$

FIG. 9. Zircon.

OLIVINE GROUP. (Bragg and Brown, 3). In forsterite, Mg_2SiO_4, (Fig. 7) each SiO_4 group is surrounded by Mg ions. There are six coordinates from each Mg to six O ions at approximately equal distances. Each O has four coordinates, three to Mg and one to Si. Fe^{II} can replace Mg, of course. Monticellite ($MgCaSiO_4$) has the same structure as olivine (Brown and West, 6). Half of the Mg ions are replaced by Ca. This results in a slight shift of certain positions on account of the larger size of Ca.

CHONDRODITE GROUP.

Norbergite	$Mg(OH, F)_2Mg_2SiO_4$
Chondrodite	$Mg(OH, F)_2(Mg_2SiO_4)_2$
Humite	$Mg(OH, F)_2(Mg_2SiO_4)_3$
Clinohumite	$Mg(OH, F)_2(Mg_2SiO_4)_4$

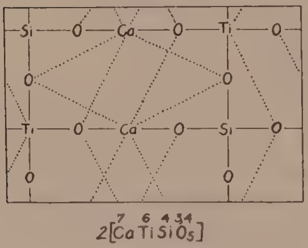
A comparison of these four minerals (Taylor and West, 8) is very interesting. They are very similar to forsterite as may be seen in Fig. 8. If we could cut forsterite parallel to (001) into slabs of Mg_2SiO_4 units and introduce layers consisting of $Mg(OH,F)_2$ at definite intervals we would arrive at the members of the chondrodite series. In norbergite slabs of Mg_2SiO_4 alternate with slabs of $Mg(OH,F)_2$, (Fig. 8). In chondrodite a *pair* of slabs of Mg_2SiO_4 is always followed by a layer of $Mg(OH,F)_2$. In humite every fourth slab would be $Mg(OH,F)_2$, in clinohumite every fifth slab. No diagrams are shown for chondrodite, humite, or clinohumite. They can, however, be easily constructed by a combination of the diagrams of forsterite and chondrodite. Each Mg in this group is linked to six anions. Where the Mg is located in a slab of $Mg(OH,F)_2$ two of the six anions are (OH,F), the other four are O. Each (OH,F) is connected to three almost equidistant Mg cations.

PHENACITE. Phenacite, Be_2SiO_4, (Bragg and Zachariasen, 7) contains BeO_4 tetrahedra besides the SiO_4 groups. Each SiO_4 group is linked to four BeO_4 groups. Fig. 7 may be used for illustrating this structure if Be is put in place of Mg. Since there exists only a single bond between each Si and Be ion, not a double bond, the missing fourth coordinates should connect with Be ions below or above the plane of the diagram. Each O has three coordinates. Willemite, Zn_2SiO_4, has the same structure, Zn taking the place of Be.

ZIRCON. In zircon, $ZrSiO_4$, (Vegard, 1, and Wyckoff and Hendricks, 2) each Zr cation is linked to eight nearly equidistant O ion. Each O ion is tied to two Zr and one Si cations. Since each

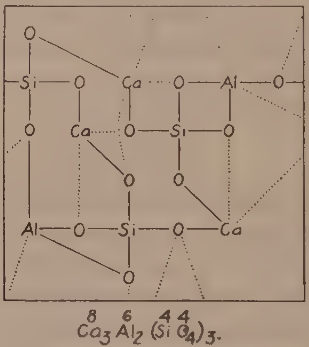
Zr is linked to eight different tetrahedra of SiO_4 only four of the eight coordinates can be shown in Fig. 9 without destroying the simplicity of the diagram.

TITANITE. In titanite, $CaTiSiO_5$, (Zachariasen, 26), each Ti ion is surrounded by six O ions at the corners of a somewhat distorted octahedron. Ca has seven coordinates to seven nearly equidistant O ions. Each O is linked to three or four cations. See Fig. 10.



$2[\overset{7}{Ca}\overset{6}{Ti}\overset{4}{Si}\overset{3,4}{O_5}]$

FIG. 10. Titanite.

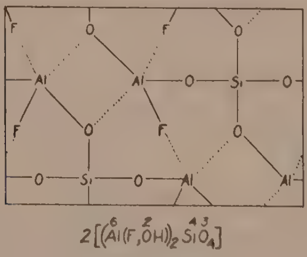


$\overset{8}{Ca_3}\overset{6}{Al_2}(\overset{4}{Si}\overset{4}{O_4})_3.$

FIG. 11. Garnet (grossularite).

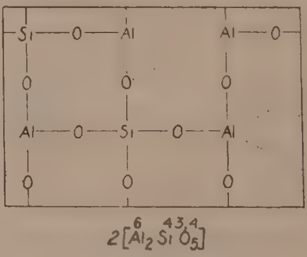
GARNET GROUP. It is difficult to represent the garnet structure (Menzer, 4) diagrammatically because the SiO_4 groups must be kept apart. In grossularite, $Ca_3Al_2(SiO_4)_3$ the SiO_4 groups are separated by Al and Ca (Fig. 11). Al has the coordination number 6 and Ca the number 8. The eight O ions around Ca are at the corners of a distorted cube. Each O in the structure has four coordinates, two to Ca, one to Al and one to Si.

TOPAZ. Topaz, $[Al(OH,F)]_2SiO_4$, also has self-contained SiO_4 groups linked together by Al ions (Pauling, 11, and Alston and West, 13). Al has six coordinates, four to O and two to (OH,F). Each (OH,F) lies between two Al but not in a straight line with



$2[(\overset{6}{Al}(F,\overset{2}{O}H))_2\overset{4}{Si}\overset{3}{O_4}]$

FIG. 12. Topaz.



$2[\overset{6}{Al_2}\overset{4}{Si}\overset{3,4}{O_5}]$

FIG. 13. Cyanite.

them. It has two coordinates while each O has three. See Fig. 12. The perfect basal cleavage in topaz seems to lie between Al,O and Al,O planes. It most probably does not cut the very strong Si-O bonds which are found everywhere in the crystal except between the two planes mentioned.

CYANITE. Cyanite, Al_2SiO_5, (Náray-Szabó, Taylor and Jackson, 19) as well as andalusite and sillimanite have self-contained SiO_4 groups linked together by Al (Fig. 13). The Al ions in cyanite have six coordinates. The O ions have three and four coordinates connecting two Al and one Si or four Al, respectively. Half of the Al ions occur in chains parallel to the *c* axis. Parallel to the plane (100) layers of ions occur in the order: Al,O—Al,O—Si,Al,O—O—Si,Al,O and repeated. The excellent cleavage of cyanite parallel (100) probably occurs between the two Al,O layers where each O is linked to four Al and not along the O layer as proposed by Náray-Szabó, Taylor and Jackson (19). The reason for this belief will be given under staurolite in the next paragraph. Too little is known about crystal physics to explain the anomalous differences in hardness on the (100) face in cyanite.

STAUROLITE. Staurolite, $Fe(OH)_2(Al_2SiO_5)_2$, may be conceived as built up of unit slabs of cyanite interlayered with slabs of Fe $(OH)_2$ (Náray-Szabó, 20). The slabs of $Fe(OH)_2$ are inserted in the cyanite structure between the two Al,O layers parallel to (100) along which the cleavage occurs in cyanite according to the writer's belief. This introduction of $Fe(OH)_2$, therefore, destroys the cleavage for staurolite. If cleavage took place along the O layer there would be no reason why it should not be found in staurolite since the O layer is preserved in the staurolite structure. Attention is called to the different orientation of the two minerals. The (100) plane of cyanite is the (010) plane of staurolite. It is not possible to show all these features in Fig. 13.

SILLIMANITE. Sillimanite, Al_2SiO_5, (Taylor, 10) differs from cyanite mainly with respect to the behavior of one half of the Al ions. These Al ions have four coordinates, the same as Si, resulting in AlO_4 groups. The other Al ions are arranged as in cyanite in chains and have a coordination of six (Fig. 14). Why is sillimanite fibrous in structure? The writer observed that the SiO_4 and AlO_4 groups, which are alternately linked together, form endless double chains of SiO_4 and AlO_4 tetrahedra parallel to the *c* axis (parallel to the fibers). Endless double chains of SiO_4 are found in amphiboles and, according to Warren, explain the fibrous structure of amphiboles and chrysotile, as discussed later. Now a double chain consisting of alternating SiO_4 and AlO_4 groups should be nearly as strong as one consisting of SiO_4 entirely and should impress its individuality upon the structure as a whole.

Mullite and sillimanite are identical in structure, according to Taylor (10), except for the fact that one O ion out of every forty O is missing in mullite. This behavior is unexplained so far.

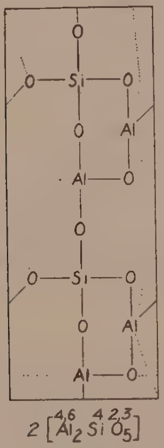


Fig. 14. Sillimanite.

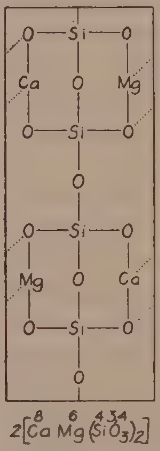


Fig. 16. Diopside.

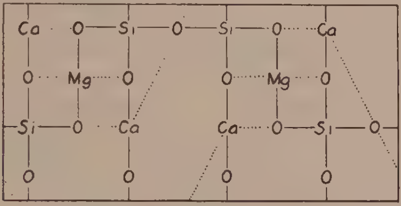
Andalusite. In andalusite, Al_2SiO_5, Taylor (23) found that one-half of the Al have six coordinates and are arranged as in cyanite and sillimanite. The other half of the Al ions possess five coordinates, which is rather unusual. Each O is linked to two Al and one Si or to three Al. Fig. 13 would illustrate this structure if the number of bonds of two Al ions were reduced from 6 to 5.

Silicates with Self-contained Aggregates of SiO_4 Groups

As the ratio of Si:O decreases below 1:4 aggregates like Si_2O_7 (Fig. 1,b), Si_3O_9 (Fig. 1,c), and Si_6O_{18} (Fig. 2) are found in the structures. Such self-contained aggregates are separated from one another by the remaining cations.

Thortveitite. Thortveitite, $Sc_2Si_2O_7$, (Zachariasen, 25) contains Si_2O_7 groups linked together by Sc. Scandium has six coordinates and is at the center of a distorted octahedron of O ions.

Melilite Group. The members of this complex group to which Warren (21) assigns the formula $(Ca,Na)_2(Mg,Al)_1(Si,Al)_2O_7$ contain the Si_2O_7 group. Al may replace a part of the Si. A structurally different Al may substitute for part of the Mg. Magnesium here has the unusual coordination number 4. Isomorphous replacement in this group, then, is very complicated. For example, if Al replaces a part of Si, Ca should replace a corresponding amount of Na. $Ca_2Al(Si,Al)O_7$ which is gehlenite (Beerman, H., *Am. Min.*, vol. **14,** p. 400, 1929) would be the result. If Ca replaced all of the Na and the amount of Si remained constant, Mg should replace all of the structurally equivalent Al resulting in ackermanite $Ca_2MgSi_2O_7$. The rare mineral hardystonite $Ca_2ZnSi_2O_7$ has the same structure as melilite (Fig. 15).



$$2\left[(\overset{8}{Ca},Na)_2\,(Mg,\overset{4}{Al})\,(Si,\overset{4}{Al})_2\,\overset{4}{O}_7\right]$$

FIG. 15. Melilite.

DANBURITE. Danburite, $CaB_2Si_2O_8$, (Dunbar and Machatski, 31) contains Si_2O_7 groups notwithstanding its apparent excess of O. This excess O ion together with three oxygen ions of three other Si_2O_7 groups forms a tetrahedron at the center of which is placed a B ion. These tetrahedra are arranged in such a way that B_2O_7 groups occur besides Si_2O_7 groups. Calcium has eight coordinates. Oxygen ions may have two, three, or four coordinates.

BENITOITE. The rare mineral benitoite, $BaTiSi_3O_9$, (Zachariasen, 27) contains Si_3O_9 groups. This explains its crystallization in the ditrigonal bipyramidal class. It would be very difficult to draw a simple diagram which would show the proper relationship of the cations. No Ba or Ti ions are inside the Si_3O_9 "ring." The "rings" are linked together by these ions, both of which have a coordination number 6. Oxygen has two and three coordinates.

BERYL. Beryl, $Be_3Al_2Si_6O_{18}$, (Bragg and West, 5) has "rings" consisting of six SiO_4 tetrahedra linked into Si_6O_{18} aggregates. These "rings" are "open," that is no cations are inside of them. They form "wide channels" through the crystal parallel to the *c* axis. It is thought that these channels may account for the inclusion of helium and other atoms in beryl. The "rings" are interlinked by Al with six coordinates and by Be with four. Oxygen has two and three coordinates. It is practically impossible to draw a satisfactory diagram of beryl with only one molecule.

SILICATES WITH ENDLESS CHAINS OF SiO_4

PYROXENE GROUP. Single endless chains of SiO_4 as shown in Fig. 3, are the characteristic structural feature of the pyroxenes (Warren and Bragg, 9). These chains are parallel to the *c* axis. The chains are connected to one another by Mg, Fe, Ca and other cations which have a coordination number of 6 or 8. (Fig. 16 diopside). The chains are spaced in such a way that projected on a plane normal to the axis of the chain they have the distribution shown in Fig. 21. Each trapezoid contains one chain seen end on. Each chain is turned 180° about its long axis with repect to its neighbors. The 87° prismatic cleavage of the mineral is produced by breaking of bonds between the chains as indicated by a heavy line in Fig. 21. The bonds between Si and O are very strong and good cleavage can develop therefore only between O and the other cations. In acmite $(Na,Fe)(SiO_3)_3$ Na replaces Ca, and Fe^{III} the Mg of the diopside molecule. No detailed investigation has been made of augite but it is practically certain that it has the diopside structure.

ENSTATITE. The orthorhombic pyroxene enstatite $(Mg,Fe)SiO_3$ (Warren and Modell, 17) is very closely related to diopside. Mg replaces Ca with only a slight shift of some of the ions. If a diopside unit cell were reflected on its (100) plane, the unit cell of enstatite would result. The enstatite unit cell, therefore, is almost twice as long in the direction of the *a* axis as the cell of diopside. This operation reminds one of twinning on a unit cell scale. It also explains the orthorhombic symmetry of enstatite.

AMPHIBOLE GROUP. The endless double chains of SiO_4 groups (Fig. 4) distinguish the amphiboles (Warren, 15 and 16) from the pyroxenes. Parts of the amphibole structure are very similar to the pyroxenes. If one could cut out certain slabs of the tremolite structure, one would obtain sections almost identical with the unit cell of diopside. In Fig. 17 of the tremolite structure, the links of the double chains have been simplified from six SiO_4 groups (as actually found) to four SiO_4 groups. This was necessary in order to produce a reasonably simple diagram. The unit of the chain, and therefore of the chemical formula, is the group Si_4O_{11} as outlined in Fig.

4. Warren (15) and Kunitz[1] independently have shown that the amphibole formula as formerly given is wrong and have substituted the formula $(OH)_2Ca_2Mg_5(Si_4O_{11})_2$ for tremolite. The O in excess of the Si_4O_{11} groups exists as (OH) in the structure. Each (OH) is linked to 3 Mg. The Mg ion is in the center of an octahedron, four of whose corners are O, the other two OH. Other interesting features in the structure are the large openings designated by "vacant position" in Fig. 17. These positions are unoccupied as long as no trivalent cation replaces a part of Si in the chain. In hornblende, $(OH,F)_2\ (Na,K,Ca,Mn)_{2-3}\ (Mg,Fe,Mn,Ti,Al)_5\ (Si,Al)_8O_{22}$, according to Warren (16) these "vacant positions" contain alkali ions when Al has replaced a part of the Si. As in melilite, the possible combinations of replacement are very numerous in hornblende and other amphiboles. Warren's paper should be consulted for details. The cleavage of the amphiboles may best be explained with the aid of a diagram similar to Fig. 21. The cleavage will pass around the double chains as indicated in Fig. 21 for single chains, but the general direction of the line now makes an angle of $(56\times\frac{1}{2})^\circ$ with the *a* axis instead of $(93\times\frac{1}{2})^\circ$.

ANTHOPHYLLITE, $(OH)_2Mg_7(Si_4O_{11})_2$, (Warren and Modell, 18) bears the same structural relationship to tremolite as enstatite to diopside. In other words, the unit cell of anthophyllite consists of the unit cell of tremolite which has been doubled by reflection on the (100) plane.

CHRYSOTILE. The structure of the chrysotile asbestos $(OH)_6Mg_6(Si_4O_{11})\cdot H_2O$ is built around the same double chains Si_4O_{11} as the amphiboles (Warren and Bragg, 32). To each chain there are attached the requisite Mg and (OH) groups. One molecule of water is also in the structure. Mg has six coordinates. Each (OH) is linked to three Mg. Each chain is linked to its neighbors by very few and relatively weak bonds which explains the fibrous structure of asbestos.

SILICATES WITH SHEETS OF SiO_4 GROUPS

W. L. Bragg (37) and Pauling (29) simultaneously proposed sheets consisting of interlinked SiO_4 groups (Fig. 5) for silicates which have excellent basal cleavage and hexagonal or pseudohexagonal symmetry. A unit of such a sheet has the formula Si_4O_{10}. All the tetrahedra of SiO_4 in a sheet point in the same direction. The size of the "meshes" in the sheet is determined by the SiO_4 groups.

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[1] Kunitz, W., *Neues Jahrb., Beil. Bd.*, **60**, A, p. 228, 1929.

Since these are practically constant the "meshes" will vary very little in different minerals containing such sheets. The sizes of the unit cells of such minerals in the *a* and *b* directions should be very similar. Mauguin (34) was the first investigator who pointed out this fact.

MUSCOVITE. In muscovite, $(OH)_2KAl_2(Si_3Al)O_{10}$, one-fourth of the Si in the Si_4O_{10} sheets is replaced by Al resulting in $(Si_3Al)O_{10}$ sheets. Adjoining sheets have their tetrahedra pointing toward each other (Fig. 22). Between the two sheets are the other Al ions which have six coordinates and the OH groups. Four coordinates of each Al link two $(Si_3Al)O_{10}$ sheets together. The other two coordinates hold the (OH) in the structure. Fig. 22 shows the succession of sheets in muscovite. As will be noticed, the K ions occur in layers between pairs of sheets and, on account of their low chemical valency, tie these sheets together but loosely. Therefore, cleavage occurs in mica along these alkali planes. Incidentally, these planes in muscovite are almost exactly one one-millionth of a millimeter apart. Fig. 18 shows muscovite diagrammatically. The part of the formula inside the SiO_4 square is a powerful link between two superimposed sheets, while the K ions would have to be imagined between these superimposed units of sheets. (Pauling, 29, and Jackson and West, 33.)

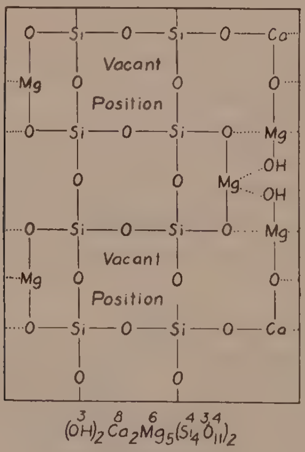

FIG. 17. Tremolite.

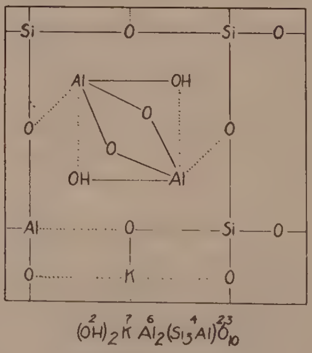

FIG. 18. Muscovite.

PHLOGOPITE. Phlogopite, $(OH)_2KMg_3(Si_3Al)O_{10}$, differs from muscovite only by a difference in structure occurring between the

SiO_4 sheets (Pauling, 29). Two Mg ions take the place of the two Al ions. The third Mg occupies a position in the same plane which had been vacant in muscovite (indicated by x in Fig. 22). This is possible because the chemical valency of $3Mg = 2Al$. In muscovite each (OH) is linked to two Al, in phlogopite each (OH) must be linked to three Mg since the number of (OH) groups remains constant. (Fig. 19).

BIOTITE does not differ from phlogopite except in the replacement of Mg by Fe.

MARGARITE. In the brittle micas (Pauling, 29), for example in margarite, $(OH)_2CaAl_2(Si_2Al_2)O_{10}$, a very similar structure exists. More Al than in muscovite is substituted in the Si_4O_{10} sheets giving $Si_2Al_2O_{10}$. Calcium replaces K. This increase in valency between pairs of sheets impairs the perfect cleavage and deprives the mineral of its elasticity.

PYROPHYLLITE. Pyrophyllite, $(OH)_2Al_2Si_4O_{10}$, belongs to the kaolin group. According to Pauling (29), it is closely related to the micas. There is no substitution at all of Al in the Si_4O_{10} sheets. The structure between sheets is exactly as in muscovite. Each pair of sheets with $(OH)_2Al_2$ between is electrically neutral, however. No alkalies but only stray valences link these units together. Therefore pyrophyllite is very soft and slippery.

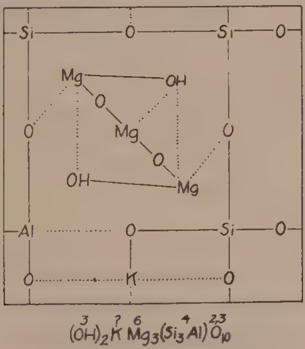

FIG. 19. Phlogopite.

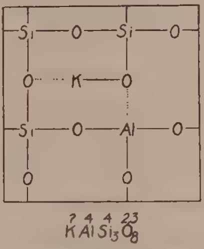

FIG. 20. Orthoclase.

TALC. Talc, $(OH)_2Mg_3Si_4O_{10}$, bears the same relation to phlogopite that pyrophyllite has to muscovite (Pauling, 29). No Al occurs in the Si_4O_{10} sheets and the Mg and (OH) groups in talc are in the same position as in phlogopite. The pairs of sheets with $(OH)_2Mg_3$ between form electrically neutral layers, resulting in softness and slippery feel of the mineral.

FELDSPAR TYPE FRAMEWORK OF SiO_4 GROUPS

The feldspar type was first predicted by Machatski (14). It consists of a framework of tetrahedra of SiO_4 (with AlO_4) linked in such a way that each O of a tetrahedron is shared by another tetrahedron (Fig. 6). Al behaves like Si in these structures. The other cations are enclosed in these tetrahedral frameworks some of which are quite "open."

FELDSPARS. Though the feldspars have been under investigation for a number of years (Schiebold, 24) their structures are only incompletely known. The chief difficulty seems to be that the Al positions can not be distinguished from Si positions since an x-ray reflection from an Al ion is about equally intense as a reflection from a Si ion. It is practically certain that Al in the feldspars has four coordinates like Si. The K, Na, or Ca ions inside the framework of tetrahedral groups probably have six or more coordinates to the O of the tetrahedra. Diagrams of the feldspars type will of necessity resemble the sheet structures since frameworks can not be shown in two dimensions. Fig. 20 is probably the simplest possible diagram for orthoclase In anorthite an Al would replace another Si and Ca would take the place of Na.

SODALITE. Sodalite, $Na_4Al_3Si_3O_{12}Cl$, consists of a framework of $Al_6Si_6O_{24}$ in which tetrahedra of AlO_4 alternate with SiO_4 groups. The structure looks similar to Fig. 6. According to Jaeger (35) and Pauling (28) the Na and Cl are inside the framework. Each Na is linked to three O and one Cl. Each Cl is held by four Na. Helvite $(Mn, Fe, Zn)_4Be_3Si_3O_{12}S$ has a similar structure in which BeO_4 groups take the place of AlO_4 in the framework.

NOSELITE, $Na_4Al_3Si_3O_{12} \cdot NaSO_4$
LAZURITE, $Na_4Al_3Si_3O_{12} \cdot (Na, Ca)SO_4$
HAÜYNITE, $Na_4Al_3Si_3O_{12} \cdot NaS_3$

These three minerals are built on the same framework as sodalite. Instead of Cl the radicals indicated above occupy a large part of the inside of the framework. They are not tightly held and substitution of one for another has been possible in the laboratory.

ANALCITE. The structure of analcite, $NaAlSi_2O_6 \cdot H_2O$, has presented many difficulties (Taylor, 22). It is certain now that it is tetragonal instead of cubic, though four investigators, including the writer, placed analcite into a cubic space group according to x-ray data. The reason for its tetragonal character is not to be found in the actual reflections that one obtains but in the fact that the 16

Na, 16 Al, 32 Si, 96 O, and 16 H_2O positions which must be put into a unit cell are an impossible stable combination in any cubic space group.

Analcite consists of a framework of SiO_4 and AlO_4 groups which is similar to those described above. The exact positions of Na which probably has six coordinates are not yet known. Each Na is linked to at least four O and probably to two H_2O. The water occurs in relatively wide channels parallel to the body diagonals of a cubic lattice. How it is held there is a matter of conjecture. The structure does not collapse when the water is driven off below 700°C (as investigated by the writer). This shows that H_2O is not an essential constituent as far as structural support is concerned. Since the mineral can also absorb this water again, the H_2O groups must be able to move rather freely in the channels described

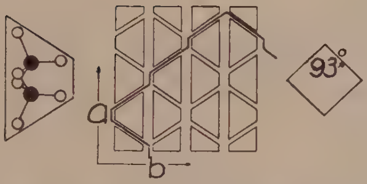

FIG. 21. Diagram explaining the reason for the position of the cleavage planes in pyroxenes, after Warren.

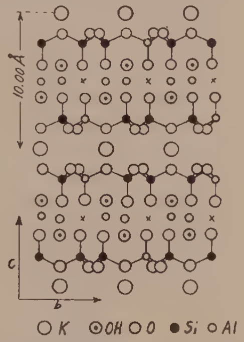

FIG. 22. Diagram showing the sequence of ionic planes in muscovite.

CONCLUSION

The structures of the silicates which have been completely investigated are reviewed. Eight types of structures exemplified by more than 30 single silicates or groups of silicates are discussed. A few observations by the writer with regard to the development of cleavage and with respect to endless double chains of alternating SiO_4 and AlO_4 groups are included. Structural diagrams for each group and certain members of these groups are shown. The purpose of these diagrams is to indicate how the ions are grouped and which of them are linked together. The diagrams are to take the place of complicated projections not easily understood by mineralogists who have had no opportunity to study actual models of the structures.

References

1. Vegard, L., *Phil. Mag.*, vol. **1,** pp. 1151, 1926; *Z. Krist.*, vol. **67,** p. 482, 1928.
2. Wyckoff, R. W. G., and Hendricks, S. B., *Z. Krist.*, vol. **66,** p. 73, 1927.
3. Bragg, W. L., and Brown, G. B., *Z. Krist.*, vol. **63,** p. 538, 1926.
4. Menzer, G., *Z. Krist.*, vol. **69,** p. 300, 1928.
5. Bragg, W. L., and West J., *Proc. Roy. Soc.*, A., vol. **111,** p. 691, 1926.
6. Brown, G., and West, J., *Z. Krist.*, vol. **66,** p. 154, 1927.
7. Bragg, W. L., and Zachariasen, W. H., *Z. Krist.*, vol. **72,** p. 518, 1930.
8. Taylor, W. H., and West, J., *Z. Krist.*, vol. **70,** p. 461, 1929.
9. Warren, B., and Bragg, W. L., *Z. Krist.*, vol. **69,** p. 168, 1928.
10. Taylor, W. H., *Z. Krist.*, vol. **68,** p. 530, 1928.
11. Pauling, L., *Proc. Nat. Acad. Sci.*, vol. **14,** p. 613, 1928.
13. Alston, N. A., and West, J., *Z. Krist.*, vol. **69,** p. 149, 1928.
14. Machatski, F., *Centralb. Min.*, A, **1928,** p. 97.
15. Warren, B. E., *Z. Krist.*, vol. **72,** p. 42, 1929.
16. " " " *Z. Krist.*, vol. **72,** p. 493, 1929.
17. " " " and Modell, D. I., *Z. Krist.*, vol. **75,** p. 1, 1930.
18. " " " and " " " *Z. Krist.* vol. **75,** p. 161, 1930.
19. St. Náray-Szabó, Taylor, W. H., and Jackson, W. W., *Z. Krist.*, vol. **71,** p. 117, 1929.
20. St. Náray-Szabó, *Z. Krist.*, vol. **71,** p. 103, 1929.
21. Warren, B., *Z. Krist.*, vol. **74,** p. 131, 1930.
22. Taylor, W. H., *Z. Krist.*, vol. **74,** p. 1, 1930.
23. " " " *Z. Krist.*, vol. **71,** p. 205, 1929.
24. Schiebold, E., *Trans. Faraday Soc.*, vol. **25,** p. 334, 1929; also *Fortschritte d. Min.*, vol. **14,** p. 62, 1930.
25. Zachariasen, W., *Z. Krist.*, vol. **73,** p. 1, 1930.
26. " " *Z. Krist.*, vol. **73,** p. 7, 1930.
27. " " *Z. Krist.*, vol. **74,** p. 139, 1930.
28. Pauling, L., *Z. Krist.*, vol. **74,** p. 213, 1930.
29. " " *Proc. Nat. Acad. Sci.*, vol. **16,** p. 123, 1930.
30. Warren, B. E., and Trautz, O. R., *Z. Krist.*, vol. **75,** p. 525, 1930.
31. Dunbar, C., and Machatski, F., *Z. Krist.*, vol. **76,** p. 133, 1930.
32. Warren, B. E., and Bragg, W. L., *Z. Krist.*, vol. **76,** p. 201, 1931.
33. Jackson, W. W., and West, J., *Z. Krist.*, vol. **76,** p. 211, 1931.
34. Mauguin, *Compt. rend.*, vol. **186,** p. 879, and p. 1131, 1928.
35. Jaeger, F. M., *Trans. Faraday Soc.*, vol. **25,** p. 320, 1929.
36. Pauling, L., *Jour. Am. Chem. Soc.*, vol. **51,** p. 1010, 1929.
37. Bragg, W. L., *Z. Krist.*, vol. **74,** p. 237, 1930.
38. Gruner, J. W., *Am. Mineral.*, vol. **14,** p. 173, 1929.

THE CHEMICAL COMPOSITION OF ROEBLINGITE

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During the mineralogical and *x*-ray investigations of the Långban minerals which are at present being carried on by Professor G. Aminoff and his associates at the Mineralogical Department of the Natural History Museum, Stockholm, there was recently discovered a mineral analogous in composition to roeblingite. For further investigation of this new mineral, a knowledge of the composition of the Franklin roeblingite is, naturally, of some interest, and, as the data we possess respecting this mineral can hardly be considered sufficient and satisfactory, a sample of roeblingite from Franklin has been made a subject of a chemical analysis.

Roeblingite has been examined and described by S. L. Penfield and H. W. Foote (*American Journal of Science*, Vol. **III**, 1897). The averages of the percentages of two analyses in close agreement carried out by the latter, and the molecular ratios calculated from them were as follows:

	Average	Mol ratios		
SiO_2	23.58	0.393	5.61	5.0
SO_2	9.00	0.141	2.01	2.0
PbO	31.03	0.139	1.99	2.0
MnO	2.48	0.035	7.43	7
CaO	25.95	0.463		
SrO	1.40	0.014		
K_2O	0.13	0.001		
Na_2O	0.40	0.007		
H_2O	6.35	0.353	5.04	5
	100.32			

By means of, as may be seen, a very general approximation of the molecular ratios, the authors succeeded in deducing the proportions $SiO_2:SO_2:PbO:RO:H_2O=5:2:2:7:5$, which gives the formula $H_{10}Ca_7Pb_2Si_5S_2O_{28}$, and, consequently, the mineral has been interpreted as being a combination of five molecules of a silicate H_2CaSiO_4, and two molecules of a basic sulphite $CaPbSO_4$. The correctness of this complex formula is, however, doubted by the authors themselves.

Concerning the execution of the analyses, there may be remarked that, although the authors themselves call attention to the fact that "*the special points of interest connected with this mineral are,* *that this is the first time that a sulphite has been observed in nature . . .* " they do not bring forward any quantitative analytical proof of that statement, but merely say that "*the odor of sulphurous anhydride may be obtained when the mineral is dissolved in a little hydrochloric acid, but this test is not very apparent.*" That the authors were too hasty in making this simple test the basis of the declaration that roeblingite is a sulphite will appear from the analysis given below, which will show that all the sulphur is combined as sulphur trioxide.

The "sulphur dioxide" was determined by the authors by dissolving a separate portion of the mineral in hydrochloric acid and bromine water, and precipitating the sulphuric acid as barium sulphate without previously removing the silica and lead from the solution. The barium sulphate precipitate, contaminated with silica and lead, was purified by fusion with sodium carbonate and reprecipitated by means of barium chloride. This method, however, is not to be considered as a very suitable one for removing these contaminations from the barium sulphate, as silica and more especially lead oxide, formed by the decomposition of lead carbonate during the fusion, will be partially dissolved by the leaching of the cake with water, as sodium silicate and sodium plumbite, respectively, and so they will be precipitated again with the sulphuric acid. In this way the authors have obtained an amount of sulphurous anhydride which is from 0.4 to 0.5 per cent too high. Recalculating this to sulphuric anhydride, the percentage is increased from 9.00 to 11.25, for which reason the percentage total of the analysis, with this correction and with an accurate value of the sulphur employed, should be about 2 per cent too high. In spite of this error, Foote has obtained an acceptable total for his analyses, which is due to the fact that the values as found by him of the basic constituents are too high.

The macroscopical and microscopical appearances of the material used by the present writer for a new analysis displayed perfect correspondence with those of the mineral described by Penfield and Foote, and it should be noted especially that, under the microscope, the mineral showed a thoroughly homogeneous structure of interwoven fibrous crystals.

One complete and two partial analyses of portions of the material were carried out by the writer. For each analysis and every separate determination there was used an amount of about 0.5 gram. The analytical methods were the following:

When the mineral was dissolved in dilute hydrochloric acid, no odor of sulphur dioxide was perceptible. However, in order to determine quantitatively minute traces which might be present, a weighed quantity of the mineral was dissolved in hydrochloric acid, under an atmosphere of carbon dioxide, and, after expulsion of the "sulphur dioxide" by boiling the solution, it was led into a measured volume of N/10 iodine-solution by means of a slow stream of carbon dioxide. No consumption of iodine could be observed in this operation, and so all the sulphur must be considered combined in the form of sulphuric anhydride.

For the determination of the sulphur trioxide, the mineral was fused with sodium carbonate, the cake leached with hot water and, after being partially neutralized with hydrochloric acid, the filtrate was cooled to the freezing-point and a current of carbon dioxide passed through the liquid until the red color of phenolphthalein disappeared. The precipitated lead carbonate was filtered off and, after acidifying with hydrochloric acid, the filtrate was evaporated to dryness, the silica separated and the sulphuric acid precipitated with barium chloride. The barium sulphate thus obtained was tested and found to be free from silica and lead oxide.

For the execution of the main analysis, the mineral was dissolved in dilute nitric acid, whereupon the silica was separated by a double evaporation to dryness. For the purpose of removing the nitric acid, the solution was repeatedly evaporated to dryness after the addition of hydrochloric acid. After evaporation, the residues were dissolved in dilute hydrochloric acid, and then there was added to the solution the residue from the evaporation of the silica with hydrofluoric acid, after which the lead was precipitated by hydrogen sulphide, and weighed as sulphate.

In the filtrate from the lead sulphide, the manganese (after the removal of the hydrochloric acid by evaporation with an excess of sulphuric acid) was separated from the strontium and the greater part of the calcium by means of sulphuric acid and ethyl alcohol. From the small amount of lime that remained, the manganese was separated by double precipitation with ammonium persulphate in the slightly sulphuric acidified ammonium-sulphate solution, whereupon the lime was precipitated as oxalate. The calcium and strontium sulphates were converted into carbonates by fusion with sodium carbonate and were dissolved in hydrochloric acid, calcium and strontium oxalates being formed. The collected precipitations of the oxalates were heated to dryness at a temperature of 100°C., and weighed as $Ca(Sr)C_2O_4 \cdot H_2O$. By means of gentle ignition they were then decomposed to carbonates, which were dissolved in nitric acid.

The nitrates were separated by treatment with amyl alcohol, and, finally, the strontium was determined as sulphate.

The determination of the alkalies was carried out according to Lawrence Smith's method. For the determination of water and carbon dioxide, there was employed a sifted powder, about 1 mm. in size, so as to avoid hygroscopical water. A portion of this prepared material, placed in a platinum vessel in a quartz tube,was heated in an electric furnace to a temperature of 1250°C., the water and carbon dioxide being carried into the absorption vessels by a current of air. By this means there were obtained the values for water and carbon dioxide reproduced in the table below. The percentage of hygroscopical water was determined by drying a finely ground portion of the mineral at 105°C. In order to ascertain if any part of the combined water was expelled at this temperature—which was likely when one considers the high value of hygroscopical water—there was also carried out a determination of water with a finely ground portion of the mineral, which gave the result that no combined water was given off at 105°C.

In the following table there are included the calculated values of the analyses, and their averages and molecular ratios.

	I	II	III	Average	Mol. ratios	A.	B.
SiO_2	23.53	23.55	23.62	23.57	0.3924	0.4063	6.03
CO_2	0.61	—	—	0.61	0.0139		
SO_3	10.78	10.82	10.84	10.81	0.1350	0.1348	2.00
PbO	29.99	30.04	30.08	30.04	0.1346		
MnO	2.48	2.50	—	2.49	0.0351	0.4743	7.04
CaO	23.15	23.09	—	23.12	0.4123		
SrO	2.77	2.80	—	2.79	0.0269		
H_2O+ 105°	6.15	—	—	6.15	0.3414	0.3414	5.06
H_2O- 105°	0.45	—	—	0.45	—	—	—
				100.03			

FeO, ZnO, BaO, MgO, K_2O, Na_2O were absent.

As the molecular ratios of SO_3 and PbO are equal, it may be considered correct to combine these constituents to $PbSO_4$, the molecular ratio of which, in column A, will then be 0.1348. It may be supposed that the small amount of carbon dioxide occurs as calcite, but it seems to the present writer more probable that this substance, too, is a constituent in the crystal-lattice of roeblingite. Furthermore, the calculation of the carbon dioxide in one way or the other does not decisively influence the formula. According to the quotients in column B, this ought to be written: $2\ PbSO_4 \cdot 7\ RO \cdot 6\ SiO_2 \cdot 5\ H_2O$; or $2\ PbSO_4 \cdot R_7H_{10}Si_6O_{24}$, where R = Ca, Si, Mn.

This formula presents several points of agreement with that stated by Penfield and Foote, and seems to be as complicated as theirs. However, in another manner of writing, the formula $2PbSO_4 \cdot R_7H_{10}(SiO_4)_6$ is obtained, which shows roeblingite to be a combination of two molecules of lead sulphate and six molecules of an "acid" Ca-Si-Mn orthosilicate, or a combination of $2PbSO_4$ with an acid Ca-Sr-Mn salt of the hypothetical acid $H_{24}Si_6O_{24}$. This interpretation of the composition of the silicate group is, from the chemical properties of the mineral—*inter alia*, no combined water is given off under a temperature of 200°C.—preferable to the theory of its being a salt with five molecules of water of crystallization of the—from a valence-chemical point of view, conceivable—acid $H_{14}Si_6O_{19}$.

There is given below, in a table, a comparison between the theoretical percentages and those actually obtained from the analyses, after replacing the carbon dioxide by its equivalent amount of silica, and strontium and manganous oxides by their equivalent amounts of lime, and recalculating to 100 per cent. The agreement between the found and the calculated values is, as will be seen, satisfactory, and confirms the correctness of the stated formula. According to its composition, roeblingite should be grouped with

	Found	Calculated for $2PbSO_4 \cdot Ca_7H_{10}Si_6O_{24}$
SiO_2	24.90	24.86
SO_3	11.03	11.04
PbO	30.65	30.80
CaO	27.14	27.08
H_2O	6.28	6.22
	100.00	100.00

haüyne and noselite, which, too, have three molecules of orthosilicates to one sulphate group.

The chemical analysis of the Långban roeblingite, as well as the *x*-ray analytical investigations of the two minerals, will be published by Professor G. Aminoff in the series "Contributions to the Mineralogy of Långban," in *Kungl. Svenska Vetenskapsakademiens Handlingar*.

BARITE AND WITHERITE FROM NEAR EL PORTAL, MARIPOSA COUNTY, CALIFORNIA

A. A. Fitch

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Location

The deposits to be described comprise a group of north-south veins outcropping on both sides of the Merced River (though more abundant to the south), near El Portal, the entrance to Yosemite National Park on the All-Year Highway. They have been traced for a mile to the north of the Merced River, and two miles to the south, while isolated exposures have been found much further afield.

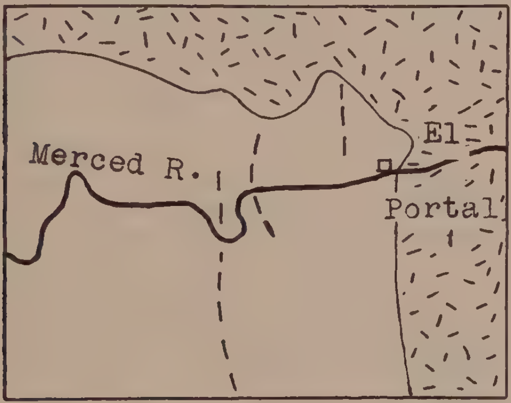

Fig. 1. Sketch map showing approximate location of the veins. Scale: 1 inch = 2 miles.

The property is worked by the National Pigments Company, who produce about seventy tons daily. It was discovered and first mined in the eighties; the Yosemite Barium Company acquired the property in 1927, and disposed of it to the present owners. The method of mining and milling has been described by Young.[1]

General Geology

The area in which the veins occur is on the western flank of the Sierra Nevada batholith, and consists of isoclinally folded sediments, dominantly argillaceous, but with some arenaceous and limestone beds. These have suffered a low-grade dynamic metamorphism, superimposed upon which is a more localized chemical and thermal metamorphism, centered around small bosses of granite revealed by erosion of the roof of the batholith. The age of the sediments is not known more precisely than that they are Palaeozoic, and the granite supposedly late Jurassic. Biotite-hornblende granodiorite is the major rock type of the boss in association with which the deposits occur: a more basic phase, a hornblende-diorite, occurs marginally and as autoliths in the granodiorite.

The veins, which vary in width up to twenty feet, dip and strike in conformity with the enclosing sediments, and all of them terminate at the margin of the granite boss. As the bosses are approached, the vein-filling changes completely in composition and texture.

Vein Filling

Barite. Barite occurs as an equigranular aggregate, the grade-size varying from one band to another, 0.1–0.5 mm. This banding lies parallel to the walls of the vein, and in occasional sections the barite grains are slightly elongated in that direction.

The finer-grained bands are generally the more impure, in that they may often contain an abundance of:

a. Rounded quartz individuals.
b. Cubes of pyrite.
c. Wedge-shaped crystals of titanite.
d. Prisms and grains of tourmaline.
e. Magnetite dust.
f. Flakes of chlorite.

Scattered through the mass of the barite, without regard for the grade size of particular bands, are:

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[1] Young, G. J., Mining and Milling Barite: *Eng. and Min. Journ. Press*, Vol. **130**, p. 70, 1930.

a. Euhedral, prismatic crystals of a pyroxene near hedenbergite, which are commonly altered in an obscure fashion to an opaque mat.
b. Ragged prisms of actinolite.
c. Witherite, occurring as interstitial, irregular stringers: clearly soluted residual fragments of large individuals.

Ore of this type forms much of the vein material in the parts distant from the granite.

So-called "horses" occurring in the ore are either of fine-grained barite, or masses of quartz-pyrite rock.

WITHERITE. Witherite occurs, as does the barite, in equigranular aggregates, about 1 mm. in grade size. It is found in restricted parts of the veins lying nearer to the granite than most of the barite, but to some extent it is intermixed with that mineral. Its associated impurities are similar to those found in the barite, and do not call for further comment, except to remark that where barite occurs, it may be locally a replacement of witherite.

In thin section, witherite is discriminated from calcite by its less perfect cleavage, extinction parallel with the best cleavage direction, the very marked change of relief on rotating the lower Nicol, and by its twinning. Witherite exhibits the usual cyclic twinning on *m* [110], whereby pseudohexagonal groups are produced: the angle $m:m'$ is 118° 30′. In addition, each individual shows polysynthetic twinning, the laminae in the three individuals of the cyclic twin making angles of approximately 120° with each other. This twinning law cannot be determined precisely from the sections available, but the twin and composition plane is apparently a face in the *c*-zone, and since both pinacoids are planes of symmetry, it follows that the twin plane is a prism. Further, since the laminae in adjacent individuals of the cyclic twin do not extinguish together, the twin plane for the polysynthetic twinning is different from that for the cyclic twinning, i.e., the twin-plane for the polysynthetic twinning is a prism other than [110]. In witherite, twinning is only conspicuous in sections perpendicular to the common *c*-axis, such sections showing very low birefringence, about 0.001. This is in marked contrast with the polysynthetic twinning of calcite, appearing in sections of widely differing orientations and birefringence.

CALC-SILICATE MINERALS. As the veins are followed toward the granite boss, there is a development of increasingly coarse calc-silicate minerals, and a corresponding diminution and finally a complete absence of barite and witherite.

The calc-silicate minerals observed are:

Andradite
Hedenbergite
Actinolite
Vesuvianite
Anorthite
Clinozoisite
Calcite

Other minerals occurring in smaller quantity are:

Quartz
Sericite
Titanite

The calc-silicate rock is roughly banded parallel with its walls, and the bands may differ widely in composition. Bands having the following constitution have been noted:

a. Calcite
b. Quartz
c. Euhedral or subhedral andradite porphyroblasts in a granular quartz matrix: a partial intergrowth of the two minerals may occur.
d. Small hedenbergite idioblasts in a granular quartz matrix.
e. Hedenbergite glomeroblasts[2] in a granular anorthite matrix.
f. Finely granular almost hornfelsic aggregate of hedenbergite and clinozoisite, with interstitial residual calcite.
g. Euhedral or subhedral andradite, and euhedral vesuvianite porphyroblasts in a quartz matrix.
h. Vesuvianite idioblasts in a quartz matrix.

Occurring in parallel growth with the hedenbergite are occasional thin prisms of a peculiar sodic amphibole, pleochroic in blue and green, with $Z \wedge c$ at least 22°, but sufficient material was not available for precise identification.

Cutting the glomeroblasts and isolated porphyroblasts of hedenbergite are ragged crystals of actinolite, growing at the expense of the hedenbergite, a change involving partial replacement of lime by iron oxide and magnesia. The hedenbergite, however, has an unusually deep green color, and it may possibly contain more iron than is indicated by the formula $CaO \cdot Fe_2O_3 \cdot 2SiO_2$. If this be assumed, the change to actinolite, $CaO \cdot 3(Fe,Mg)O \cdot 4SiO_2$, becomes almost a simple paramorphism. Certainly there is no petrological evidence of addition or subtraction of material during the change.

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[2] The term 'glomeroblast' is adopted here for convenience of description of a fairly common contact metamorphic rock texture for which no adequate term exists. A 'glomeroblast' is defined as a porphyroblast, in which the unit is not a single individual, but an aggregate of grains. 'Glomeroblastic' is thus a metamorphic rock texture corresponding to the glomeroporphyritic texture of igneous rocks in the same way as porphyroblastic corresponds with porphyritic.

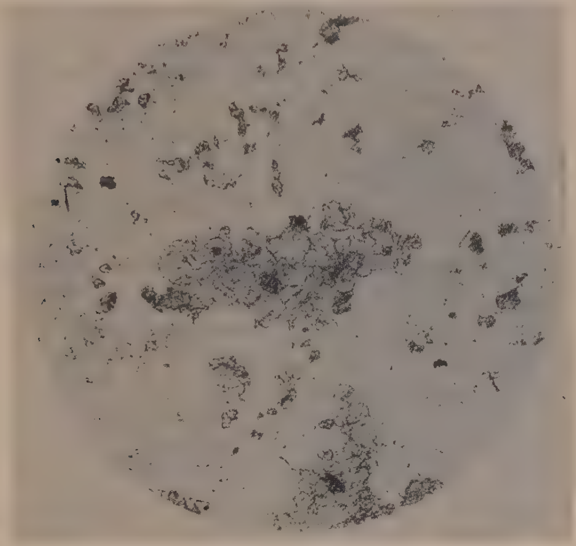

FIG. 2. Photomicrograph showing a "glomeroblast" composed of granular hedenbergite in a matrix of granular anorthite.

SURFICIAL PRODUCTS

The calc-silicate minerals are little affected by the action of meteoric waters. Barite, also, is unchanged, though a small amount of redistribution and recrystallization has taken place.

When the witherite-pyrite-quartz ores are subjected to the action of meteoric waters, the pyrite first oxidizes and hydrates to limonite, with the production of sulphuric acid.

$$\underset{\text{Pyrite}}{4FeS_2} + 15\ O_2 + 8H_2O = \underset{\text{Limonite}}{2Fe_2O_3} + 8H_2SO_4$$

The sulphuric acid then attacks the witherite with production of barite

$$\underset{\text{Witherite}}{BaCO_3} + H_2SO_4 = \underset{\text{Barite}}{BaSO_4} + H_2O + CO_2$$

Hence there result two kinds of product from this surficial oxidation and hydration:

a. An earthy aggregate of limonite and finely crystalline barite in small tabular crystals.

b. Barium sulphate has sometimes migrated from its place of origin, and produced stalactitic clusters of barite crystals. It is possible that it was calcium sulphate which was first formed by reactions with calcite similar to those outlined above for witherite, and that the calcium salt migrated and reacted with witherite to produce the barite found in stalactites.

As the barite crystals in this surficial material increase in size, they show a peculiar change of habit.

a. Microscopic crystals, about 0.1 mm. in diameter, are flat and tabular with [001] and [110].

b. The smaller macroscopic crystals, of 1 or 2 mm. diameter, are equidimensional with the same faces.

c. Crystals of larger size, up to 2 cms. in diameter, reveal an increasing tendency to round off the obtuse angle between the prism faces, and to have irregular stepped faces.

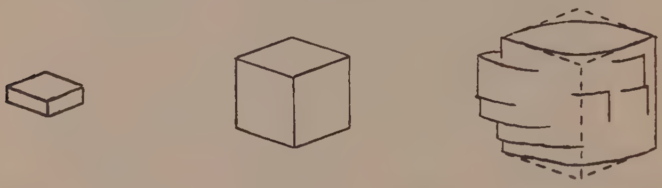

FIG. 3. Showing change of habit with increasing size of barite crystals.

WALL ROCKS

It has already been noted that the wall rocks of the vein consist everywhere of metamorphosed sediments, and that the veins nowhere cut the granite.

Two types of argillaceous wall rocks may be recognized:

a. Calcareous

b. Graphitic

At considerable distances from the granite boss, the wall rocks have suffered but a mild dynamic metamorphism, and are calcareous or graphitic slates. However, as the granite is approached, the calcareous slate is converted to a quartz-biotite hornfels, banded with quartz, and then passes through various stages of contortion, finally becoming a homogeneous, highly siliceous hornfels. Concomitantly, the graphitic slate develops spots which become progressively larger until they are recognizable as distinct chiastolite individuals and they in turn increase in size as the contact is approached. Close to the contact, however, the chiastolite breaks down, yielding a mica-schist with predominant muscovite.

GENESIS

The evidence presented in the foregoing sections all indicates that the deposits are formed by replacement of a bed of limestone by barium solutions given off from the underlying Sierra Nevada granite batholith. The palimpsest features pointing to replacement are summarized below.

PETROLOGICAL.

a. Relics of bedding.
b. Relics of detrital mineral grains in the ore: tourmaline, sericite and titanite.
c. The presence of calc-silicate minerals in the ore.
d. The lateral gradation into calc-silicate rocks.

One specimen was obtained which shows very clearly the course of the mineralization. It is a crystalline limestone, in which the calc-silicate stage is represented by the growth of rounded quartz individuals and hedenbergite idioblasts. The remaining calcite has been replaced successively by witherite and barite. This one specimen epitomizes the history of the deposit, which may be stated thus:

a. Hypothermal.
    Formation of andradite, hedenbergite and other calc-silicate minerals.
b. Mesothermal.
    Conversion of hedenbergite to actinolite.
    Introduction of quartz, pyrite and chalcopyrite.
    Replacement of calcite by witherite.
    Replacement of calcite by barite.
    Replacement of witherite by barite.
c. Surficial.
    Conversion of pyrite to limonite.
    Conversion of witherite to barite with the formation of small stalactites.

It is interesting to note that the granites from this province may carry rather high percentages of barium: thus one from Agua Fria Creek carries 0.10% (quoted by Washington, *Chemical Analyses of Igneous Rocks*, pp. 228–9). A specimen of granite near the contact on the strike of the lode gave only a trace of barium, which suggests that the deposits, though near the contact, arise from a more deepseated source within the batholith.

STRUCTURAL.

It was the structural evidence that gave the first clues in the field to the mode of origin of the deposit. Thus the veins nowhere transgress the strike of the isoclinally folded beds; the dip of the veins is high (usually about 80°) according with the dip of the enclosing rocks. In one case, a little south of the Merced River, the vein has been traced downwards to the bottom of one of the isoclinal folds, where it turns sharply upwards, and is soon pinched out.

METAMORPHIC ZONES

It is possible to correlate the nature of the vein filling with the degree of contact metamorphism of the two types of slate constituting the wall rocks, as shown in the following table. The distances given refer to the vein forming the core of the ridge running north-south a little to the east of the mill.

Graphitic slate	Calcareous slate	Limestone	Approximate distance from contact
Mica-schist	Quartz-biotite hornfels in several degrees of flexing or contortion	Andradite-hedenbergite rock	50 yards
Chiastolite slate	Quartz-biotite hornfels	Crystalline limestone	200 yards
Graphitic slate with incipient chiastolite	Phyllite	Witherite dominant	1000 yards
Slate	Slate	Barite dominant	

SUMMARY

A group of barite-witherite veins is described, which have arisen by replacement of a bed of limestone constituting part of an isoclinally folded series of Palaeozoic sediments. All gradations are found in these limestone bands from pure barite or witherite to coarse andradite-hedenbergite and other calc-silicate rocks as the margin of a small granite boss is approached.

ON THE PRESENCE OF BERYLLIUM IN MILARITE

CHARLES PALACHE,

Contributions from the Department of Mineralogy and Petrography, Harvard University, No. 81.

Two recent papers[1] have called attention to the probability that the element beryllium is more widely distributed in minerals and rocks than has been recognized. The fact that beryllium, unless particularly sought by the analyst, is determined with the alumina in silicate analysis, makes it easy for its presence to be overlooked.

E. K. Gedney, a student in this laboratory during the year 1929–30, investigated the distribution of beryllium in a large number of minerals by spectroscopic methods, checked in some cases by chemical analysis. His interesting results are not yet ready for publication as a whole; but as one product of the study the following analysis showing that beryllium is an essential constituent of the mineral milarite seems worthy of record. Gedney found strong lines of the element in spectrograms of milarite and his analysis, for beryllium only, showed nearly 5 per cent of BeO present.

A sample of milarite was prepared by H. Berman. He found that it was practically impossible to separate milarite from adularia with which it is intimately associated; not only are they so nearly of the same specific gravity that they fail to separate in the heavy solution; but their refractive indices are so nearly identical that no satisfactory estimate of relative purity of a powder was possible under the microscope. He therefore picked out by hand fragments of clear crystals, obtaining a sample of 0.4 gram. This was analyzed by F. A. Gonyer, the result, except for the beryllium found, confirming earlier analyses. The separation of aluminum from beryllium was effected by the use of 8–hydroxyquinoline (oxin) as described in Hillebrand and Lundell, Applied Inorganic Analysis, p. 114, 1929.

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[1] C. Palache and L. H. Bauer, On the occurrence of beryllium in the zinc deposits of Franklin, N. J.: *American Mineralogist*, **15**, 30, 1930. H. S. Washington, Beryllium in minerals and rocks: *Idem.*, **16**, 37, 1931.

Analysis of Milarite

	Per cent	Molecular ratios	
SiO_2	71.66	1.19	$=24\times.050$
Al_2O_3	4.68	.046	$=1\times.046$
BeO	5.24	.209	$=4\times.052$
CaO	11.70	.209	$=4\times.052$
K_2O	4.91	.052	$=1\times.059$
Na_2O	0.46	.007	
H_2O+	1.02	.057	$=1\times.057$
H_2O-	0.05		
	99.72		

These figures show a satisfactory ratio except for a slight deficiency of alumina. They may be expressed by the formula $K_2Ca_4(Be_4Al_2Si_{24})O_{60}+H_2O$ which differs from that generally given for milarite chiefly in that one molequivalent of aluminum is replaced by beryllium and that the water is expressed in separate form. This seems to be a good illustration of the type of formula demanded by the "felspattypus" structure recently proposed by Machatschki.[2] The so-called disilicates and polysilicates of the Dana classification probably belong to this structural type which receives its name from feldspar, the most important member of the group. For example, the formula of petalite, expanded for comparison, may be written:

petalite	$Li_6\ Al_6$	Si_{24}	O_{60}
milarite	$(K_2Ca_4)(Be_4Al_2)$	Si_{24}	$O_{60}+H_2O$

This does not mean, of course, that the two minerals should be necessarily isomorphous; but it does imply that they are structurally related, the type being defined by the ratio $(Be+Al+Si):O=1:2$. The extent to which Be or Al or both replace Si in this ratio determines the amount of alkali or calcium present.

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[2] F. Machatschki, Zur Frage der Struktur und Konstitution der Feldspate: *Centralblatt für Mineralogie*, A, 97, 1928.

NOMINATIONS FOR OFFICERS OF THE MINERALOGICAL SOCIETY OF AMERICA FOR 1932

The Council has nominated the following for officers of the Mineralogical Society of America for the year 1932:

PRESIDENT: Alexander N. Winchell, University of Wisconsin, Madison, Wisconsin.

VICE-PRESIDENT: Joseph L. Gillson, E. I. du Pont de Nemours & Co., Wilmington, Delaware.

SECRETARY: Frank R. Van Horn, Case School of Applied Science, Cleveland, Ohio.

TREASURER: Waldemar T. Schaller, United States Geological Survey, Washington, D.C.

EDITOR: Walter F. Hunt, University of Michigan, Ann Arbor, Michigan.

COUNCILOR (1932–1935): William J. McCaughey, Ohio State University, Columbus, Ohio.

The twelfth annual meeting of the Society will be held December 29–31, 1931, at the Hotel Mayo, Tulsa, Oklahoma. It is planned to publish in the December issue of the Journal a *preliminary* list of papers to be presented before the Society at its annual meeting. In order to appear on the advance program, titles of papers should be in the hands of the Secretary by *November 10.*

FRANK R. VAN HORN, *Secretary*

BOOK REVIEWS

UEBER DEN UNTERSCHIED VON MINERALIEN UND LEBEWESEN, ARRIEN JOHNSEN. IV+41 pages, with 12 illustrations. Gebrüder Borntraeger, *Berlin,* 1930.

This interesting public address, given by Professor Johnsen of the University of Berlin before the Prussian Academy of Sciences, is a valuable contribution to the question of the essential differences between minerals and life forms.

E. H. KRAUS

GRENZFRAGEN DES LEBENS, FRIEDRICH RINNE. VII+128 pages, with 119 illustrations. Quelle and Meyer, *Leipzig,* 1931.

In a masterly manner, Professor Rinne, for many years the distinguished director of the Mineralogical Laboratory of the University of Leipzig, marshals observations and facts dealing with the problem of the fundamental nature of inorganic and organic substances. His acknowledged high scientific standing and zeal for investigation fit him admirably for a study of this character. The text should appeal strongly to all interested in the consideration of these fascinating borderline questions. The book is excellently printed and illustrated.

EDWARD H. KRAUS

FLÜSSIGE KRISTALLE UND LEBEWESEN, Reinhard Brauns. XI+111 pages. E. Schweizerbart'sche Verlagsbuchhandlung, *Stuttgart*, **1931.**

This volume gives a most comprehensive and worthwhile survey of the literature dealing with liquid crystals and life forms, for it contains abstracts of the 172 articles dealing with these subjects that have appeared during the last fifty years in the *Neues Jahrbuch* and the *Centralblatt für Mineralogie, Geologie and Paleontologie.* In an introduction of seven pages, Professor Brauns reviews briefly the historical development of this field of investigation and naturally emphasizes the pioneer contributions of Lehmann.

Edward H. Kraus

SPECTRUM ANALYSIS IN MINERALOGY. A. A. Fitch. 52 pages. Adam Hilger, Ltd., 24 Rochester Place, Camden Road, *London*, **1931**. Price, 1*s* 9*d*.

Inasmuch as spectrum analysis is occasionally used as an accessory means of identifying mineral species, this small pamphlet will be found extremely helpful. The author summarizes the technique to be employed in making the tests, and both qualitative and quantitative methods are referred to as well as the application of these methods to rock analysis and meteorites. Twenty-four pages are devoted to a summary of the results obtained on minerals that have been spectroscopically analyzed. The booklet concludes with a bibliography of 91 papers dealing with articles on spectrum methods.

W. F. H.

NEW MINERAL NAMES

Maitlandite

Edward S. Simpson: Contributions to the Mineralogy of Western Australia. *Proc. Roy. Soc. W. Australia*, **16,** 33–35, 1930–31.

Name: In honor of A. Gibb Maitland, Government Geologist of Western Australia from 1896–1926. Previously described as mackintoshite (*Ann. Rept. Geol. of W. A.*, **1911,** *Geol. Surv. Bull., No.* **48,** 1912; *Jour. Nat. Hist. Sci. Soc. W. A.*, **4,** 1912).

Chemical Properties: A hydrous silicate of lead, calcium thorium and uranium, $2(Pb, Ca)O. 3ThO_2. 4UO_2. 8SiO_2. 23H_2O$. Analyses: UO_3 tr, tr; UO_2 35.40, 35.60; ThO_2 25.86, 24.72; SiO_2 14.62, 16.19; Ce_2O_3 0.10, 0.10; Yt_2O_3—, 0.25; PbO 6.04, 7.90; FeO 1.57, 0.20; MnO—, 0.07; CaO 6.02, 1.28; MgO—, 0.15; H_2O+ n.d., 12.04; H_2O- n.d., 0.88; $(Ta, Cb)_2O_5$—,.67.

Physical and Optical Properties: Color black. Luster vitreous. Amorphous. $G=4.31–4.45$.

Occurrence: At Wodgina, W. Australia. By weathering passes into pilbarite and finally into hydrothorite.

W. F. F.